DISPOSAL OF OILFIELD WASTES BY LANDTREATMENT: EFFECTS ON THE ENVIRONMENT AND IMPLICATIONS FOR FUTURE LAND USE, 1986 RESEARCH PROJECT

By

R.M. Danielson, N. Okazawa, E. Peake
Kananaskis Centre for Environmental Research
The University of Calgary

And

W.J. Ceroici
Groundwater Protection Branch
Alberta Environment

A report prepared for
The Canadian Petroleum Association
and Environment Canada

June 1987

CANADIAN PETROLEUM ASSOCIATION

DISPOSAL OF OILFIELD WASTES BY LANDTREATMENT: EFFECTS ON THE ENVIRONMENT AND IMPLICATIONS FOR FUTURE LAND USE, 1986 RESEARCH PROJECT

by

R. M. Danielson, N. Okazawa, E. Peake
Kananaskis Centre for Environmental Research
The University of Calgary

and

W.J. Ceroici
Groundwater Protection Branch
Alberta Environment

A report prepared for
The Canadian Petroleum Association
and Environment Canada

June 1987

92-02790/

ACKNOWLEDGEMENTS

Sites were provided by Anric Reclaimers Limited (Brooks), Nalcan Cleaning and Disposal Limited (Grande Prairie), Pembina Oilfield Separators Limited (Drayton Valley) and Husky Oil (Lloydminster). Funding was provided by the Canadian Petroleum Association and management by Environment Canada. The authors appreciate the contributions of D. McCoy and R. Scroggins of these organizations. Research at the Kananaskis Centre was coordinated by D. Parkinson. Local site operators, Les Head and Bob Barker, and Jim Cunningham (Petro Canada) and Andy Pool (Pan Canadian) provided valuable assistance in arranging the field phase of the program. Special thanks are due to Garry Lorenz and Randy Evanchuk of Husky Oil who arranged for much of the necessary field work at Lloydminster. Soil and plant analyses were provided by the Soil Protection Branch, Lethbridge laboratory of Alberta Environment and we appreciate the cooperation and speedy analyses via Gerry Lutwick and Craig Palmer. Doug Connery provided much useful information on the field work and past analytical techniques. Expert technical assistance was provided by Carol Anderson and Kaoru Saito. The report was rapidly and expertly prepared and typed by Lynn Ewing.

EXECUTIVE SUMMARY

Landtreatment sites at Lloydminster and Drayton Valley that had been established in 1982 were assessed in 1986 for residual waste oil in the soil, soil productivity, inorganic soil chemical factors and the potential for plant uptake of undesirable organic compounds and heavy metals. Sites at Grande Prairie and Brooks were studied less intensively. All four sites were planted in June 1986 with crops appropriate to each area, barley at Lloydminster, hay at Drayton Valley and Grande Prairie and dryland pasture species at Brooks. Plant growth in all treatments at all sites were assessed visually in the fall and quantitative assessments of selected treatments were done at Lloydminster and Drayton Valley.

Growth of barley at Lloydminster ranged from poor to excellent but did not strictly reflect the amounts of oily wastes that had been applied to the plots. Growth did not appear to be influenced by past cultivation or fertilization treatments. Although the pattern of barley growth was not strongly correlated to the total sludge applied, the residual oil in the soil was a major factor influencing crop yield. Average residual oil contents ranged from 2.6 to 8.6%. Barley usually grew well when the oil content was less than 3.5%, and growth was invariably poor when the oil content exceeded 5%. The presence of soluble salts, especially chloride, also appeared to have adverse effects on plant growth which complicated the residual oil-crop yield relationship. Although oil content and chloride did adversely affect plant growth, very good growth did occur on certain plots which had received large quantities of sludge, illustrating that sites used for land treatment can potentially be reclaimed.

Oily sludge decomposition has proceeded at uneven rates in the Lloydminster plots, as plots which had received similar quantities of sludge in the past were found to contain quite different residual oil

concentrations in 1986. The causes for the different rates of decomposition were not apparent but further research might discover the controlling mechanisms which could then be used to hasten site rehabilitation.

Growth of hay at Drayton Valley ranged from poor to good and was strongly correlated to both total sludge application rates and residual oil contents. Salt concentrations were much lower at Drayton Valley than at Lloydminster and posed no problems to rehabilitation of that site. Good growth of hay occurred when the oil content was less than 3%, and poor growth occurred when oil levels exceeded 4%.

Plant growth at Grande Prairie and Brooks was generally poor and no clear conclusions could be drawn about treatment effects. As perennial species were planted at these sites, observations in subsequent years are necessary to determine the effects of land treatment.

When barley and alfalfa were grown in soils taken from the four sites and placed in the greenhouse somewhat different patterns of growth were observed than were found in the field studies. Barley grew moderately well in all the soil treatments even though growth had been poor in the field in some cases. This may have been due to the use of a different variety of barley in the greenhouse than was used in the field. In contrast, alfalfa was more sensitive to chemical stresses and mirrored results obtained in the field.

The chemical composition of the residual oil at Lloydminster was determined to be 15-18% asphaltenes, 43-50% resins, 16-23% aliphatics and 11-16% aromatics. Attempts to further resolve the chemical nature of the aromatic fraction were unsuccessful. The asphaltenes did not appear to be accumulating in the soil even though this fraction is one of the least biodegradable components of the oil.

Straw from two plots at Lloydminster was analysed for uptake of aromatic hydrocarbons that could adversely affect the use of crops grown on oil treated soils. Results of the analysis did not indicate

that any uptake and retention had occurred; however, the analytical techniques require further refinements before definite conclusions concerning plant uptake of undesirable chemicals can be reached.

Groundwater wells and piezometers were installed on the Lloydminster site to determine surficial geology, monitor groundwater flow patterns, groundwater depths and possible contamination of the groundwater. Preliminary results of these studies are available at this time. The plots are underlain by relatively low permeability silty clay till to a depth of at least 9 m. Fractures were detected in the till to a depth of about 2.5 m.

The predominant direction of shallow groundwater flow is to the east-northeast. Shallow groundwater beneath and down gradient from the plots is contaminated, primarily with inorganic constituents, especially chloride and nitrate and possibly lead. The contamination of chloride decreased rapidly with depth. Surface water was contaminated with chloride, nitrate and sulphate.

TABLE OF CONTENTS

		Page
ACKNOWLEDGEMENTS		i
EXECUTIVE SUMMARY		ii
TABLE OF CONTENTS		v
LIST OF TABLES		vii
LIST OF FIGURES		ix
LIST OF APPENDIX TABLES		xi
1.	INTRODUCTION	1
2.	OVERALL STUDY OBJECTIVES	4
3.	PRODUCTIVITY OF SOILS TREATED WITH OILY SLUDGES	5
3.1	Objectives	5
3.2	Materials and Methods	5
3.2.1	Field assessments	5
3.2.1.1	Planting of landtreatment field sites	5
3.2.1.2	Field assessments of crop growth	5
3.2.1.3	Soil sampling	7
3.2.1.4	Soil physical and chemical analysis	9
3.2.1.5	Plant nutrient and heavy metal analysis	9
3.2.2	Greenhouse assessments of soil productivity	9
3.3	Results	10
3.3.1	Crop growth	10
3.3.1.1	Visual estimates of growth at Lloydminster	10
3.3.1.2	Visual estimates of growth at Drayton Valley	13
3.3.1.3	Visual estimates of growth at Grande Prairie	13
3.3.1.4	Visual estimates of growth at Brooks	18
3.3.1.5	Quantitative estimates of crop growth at Lloydminster and Drayton Valley	18
3.3.2	Crop nutrient and heavy metal contents	21
3.3.3	Soil analyses	21
3.3.4	Greenhouse productivity assessment	27
3.4	Discussion	34
4.	OIL CONTENT, CHEMICAL ANALYSES AND PLANT UPTAKE.	37
4.1	Objectives	37
4.2	Materials and Methods	37
4.2.1	Sample collection	37
4.2.1.1	Soil samples	37
4.2.1.2	Plant samples	37

TABLE OF CONTENTS (continued)

		Page
4.2.2	Sample preparation	38
4.2.2.1	Soil samples	38
4.2.2.2	Plant samples	38
4.2.3	Sample extraction	38
4.2.3.1	Extraction for oil content measurement	38
4.2.3.2	Extraction for chemical analysis	38
4.2.3.3	Extraction for plant uptake analysis	38
4.2.4	Sample fractionation	39
4.2.4.1	Fractionation for chemical analysis	39
4.2.4.2	Fractionation for plant uptake analysis	40
4.2.5	Sample analysis	41
4.2.5.1	Oil content analysis	41
4.2.5.2	Chemical analysis	41
4.2.5.3	Plant uptake analysis	41
4.2.6	Asphaltene precipitation	42
4.3	Results	43
4.3.1	Residual oil contents of the soil	43
4.3.1.1	Lloydminster	43
4.3.1.2	Drayton Valley	43
4.3.2	Productivity versus oil content	43
4.3.2.1	Lloydminster	43
4.3.2.2	Drayton Valley	48
4.3.2.3	Generalized relationship between oil content and plant growth	48
4.3.3	Degradation of the oil	53
4.3.3.1	Lloydminster	53
4.3.3.2	Drayton Valley	53
4.3.4	Chemical analyses of the oil	53
4.3.5	Plant uptake	57
4.3.6	Asphaltene content	58
4.4	Discussion	58
4.4.1	Oil and asphaltene contents	58
4.4.2	Chemical analysis	61
4.4.3	Plant uptake	61
5.	GROUNDWATER AND SURFACE WATER STUDIES	63
5.1	Objectives	63
5.2	Methods and Materials	63
5.3	Results and Discussion	63
5.3.1	Geology	63
5.3.2	Groundwater flow	66
5.3.3	Chemistry	69
5.3.3.1	Sludge composition	69
5.3.3.2	Groundwater chemistry	69
5.3.3.3	Surface water chemistry	72
5.4	Conclusions	77

TABLE OF CONTENTS (continued)

		Page
6.	RECOMMENDATIONS FOR FUTURE WORK	78
7.	LITERATURE CITED	80
8.	APPENDIX TABLES	81

LIST OF TABLES

		Page
1.	Planting of landtreatment sites in 1986	6
2.	Visual estimates of plant vigor and growth of Bonanza barley on the Lloydminster site (September 4, 1986).	11
3.	Visual estimates of plant vigor and growth of hay mixture (primarily timothy) on the Drayton Valley site (September 16, 1986).	14
4.	Visual estimates of plant vigor and growth of alfalfa and timothy on the Grande Prairie site (1986 September 23).	16
5.	Visual estimates of plant vigor and growth of dryland pasture species on the Brooks land treatment site (October 8, 1986).	19
6.	Primary production of Bonanza barley grown on oily sludge treated soils at Lloydminster	22
7.	Primary production of a timothy-alfalfa hay grown on oily sludge treated soils at Drayton Valley.	22
8.	Nutrient concentrations in barley straw grown in oily sludge treated soils at Lloydminster.	23
9.	Nutrient concentrations in a timothy-alfalfa hay grown in oily sludge treated soils at Drayton Valley.	24
10.	Heavy metal content ($\mu g \cdot g^{-1}$) of barley straw grown on Lloydminster soil treated with oily sludges. .	25
11.	Nitrogen and phosphorous status of soils treated with oily sludges at Lloydminster.	25
12.	Chemical and moisture characteristics of soils treated with oily sludges at Lloydminster.	26
13.	Cation and anion concentrations in saturated extracts of soils treated with oily sludges at Lloydminster. .	28
14.	Nitrogen and phosphorous status of soils treated with oily sludges at Drayton Valley.	29

LIST OF TABLES (continued)

		Page
15.	Chemical and moisture characteristics of soils treated with oily sludges at Drayton Valley.	30
16.	Cation and anion concentrations in saturated extracts of soils treated with oily sludges at Drayton Valley.	31
17.	Germination and emergence of Diamond barley and Rambler alfalfa grown in the greenhouse on soils previously treated with oily sludges in the field.	32
18.	Yield of Diamond barley and Rambler alfalfa grown in the greenhouse on soils previously treated with oily sludges in the field.	33
19.	Relation between dry weights of barley and the soil's corresponding oil content at the Lloydminster site . .	46
20.	Relation between dry weights of hay and the soil's corresponding oil content at the Drayton Valley site..	49
21.	Degradation of oil at the Lloydminster site since October 1985	54
22.	Degradation of oil at the Drayton Valley site since October 1984..	55
23.	Asphaltene contents of each subplot of the Lloydminster site.	59
24.	Water level data	67
25.	Inorganic and metals composition of sludges.	70
26.	Groundwater chemistry before sludge application . . .	71
27.	Comparison of 86/09/10 groundwater analysis to C.D.W.S.	75
28.	Analysis of pond water prior to sludge application. . .	75

LIST OF FIGURES

		Page
1.	Plot arrangement and treatments of oily sludge, fertilizer, and cultivation at the four landtreatment sites, 1982-1985.	2
2.	Barley in Lloydminster plot 1W in foreground and 1E in background September 4, 1986.	12
3.	Barley in Lloydminster plot 5W in foreground and 5E in background September 4, 1986. Surface water runoff pond directly in front of gate.	12
4.	Timothy hay in Drayton Valley plot 3N in foreground and 3S down slope September 16, 1986.	15
5.	Timothy hay in Drayton Valley plot 6N in foreground and 6S down slope September 16, 1986.	15
6.	Alfalfa and timothy at Grande Prairie in plots 4N in foreground and 4S in background September 23, 1986. .	17
7.	Alfalfa and timothy at Grande Prairie in plot 6N in foreground and 6S in background September 23, 1986. .	17
8.	Dryland pasture grass at Brooks in plot 3S in foreground and 3N in background October 8, 1986.	20
9.	Dryland pasture grass at Brooks in plot 8S in foreground and 8N in background October 8, 1986.	20
10.	An overall view of the sludge and fertilizer application, oil contents and growth assessment at the Lloydminster site.	44
11.	An overall view of the sludge and fertilizer applications, oil contents and growth assessment at the Drayton Valley site.	45
12.	Dependency of plant productivity on the corresponding oil content of the soil at the Lloydminster site. . .	47
13.	Dependency of plant productivity on the corresponding oil content of the soil at the Drayton Valley site. .	50
14.	Approximate correlation between observed growth of barley and soil oil content based on Lloydminster data.	51

LIST OF FIGURES (continued)

		Page
15.	Approximate correlation between observed growth of hay and soil oil content based on Drayton Valley data.	52
16.	Distribution of asphaltenes, resins, aliphatics, and aromatics in three Lloydminster residual oils. . . .	56
17.	Site of Lloydminster oily sludge treatment plots. Site indicated by star.	64
18.	Plan of Lloydminster oily sludge treatment plots and locations of wells and piezometers.	65
19.	Groundwater level fluctions and precipitation at Lloydminster.	68
20.	Areal distribution of chloride and nitrate concentrations in shallow groundwater.	73
21.	Chloride concentrations in groundwater at different depths at Lloydminster.	74
22.	Chloride, nitrate, and sulphate concentration variations in runoff pond water at Lloydminster.	76

APPENDIX TABLES

		Page
1.	Electrical conductivity (E.C.), sodium adsorption ratio (SAR) and chloride, sodium, and sulphate concentrations in saturated extracts of individual samples from Lloydminster oily sludge plots. . .	82
2.	Monitoring Well Completion Information	83
3.	Groundwater Protection Branch Drill Hole Log, June 4, 1986	84
4.	Groundwater Protection Branch Drill Hole Log, December 3, 1986	86
5.	Core Description Test Hole #493.	89
6.	List of Chemical Parameters and Preservation Techniques	90
7.	Lloydminster Groundwater Chemistry: Routine Parameters	91
8.	Lloydminster Groundwater Chemistry: Organics, Metals and Nutrients	92

1. INTRODUCTION

The disposal by environmentally sound and economically feasible means of large amounts of oily wastes generated during the production of heavy oil in Western Canada is an ongoing problem which is being addressed by both the industry and by government agencies. In excess of 100,000 m^3 of these waste oils and sludges are produced each year in Alberta alone. Traditional methods of disposal such as landfilling and road oiling have produced adverse environmental effects whereas incineration because of the water and solids content of the sludges is likely to be expensive. Landtreatment seems an attactive alternative.

The short-term efficiency of landtreatment in the degradation of oily sludges and the environmental effects have been studied in a research program sponsored by the Canadian Petroleum Association and Alberta Environmental Research Trust (Peake et al. 1984, 1985; Peake and Connery 1986). During the first 4 years of the program the degradation of sludges from private reclamation plants in Grande Prairie, Drayton Valley and Brooks, as well as a mixture of sludges from Lloydminster, were studied for 1 year in laboratory experiments and for up to 4 years in field trials. The design of the field experiments is given in Figure 1. In field experiments over 68% of the light oils contained in the Grande Prairie sludge degraded during the first summer and 86% during a 3 year period. The heavy Lloydminster oil degraded more slowly, 21% over 6 months in the laboratory and 48% over 4 years in the field. At Drayton Valley about 130,000 kg of oil per ha were degraded during the first summer after sludge application. Degradation rates were lower after subsequent sludge applications. No statistically significant differences in degradation rates were found with nutrient applications of 230 kg N/ha or 460 kg N/ha or with cultivation rates of once every 2 weeks or once every 4 weeks.

The oil did not penetrate the soil below the 15-30 cm mechanical mixing zone and there was no contamination of groundwater or surface run-off water with oil or organic compounds. Some contamination of groundwater and surface water by chloride and nitrate was

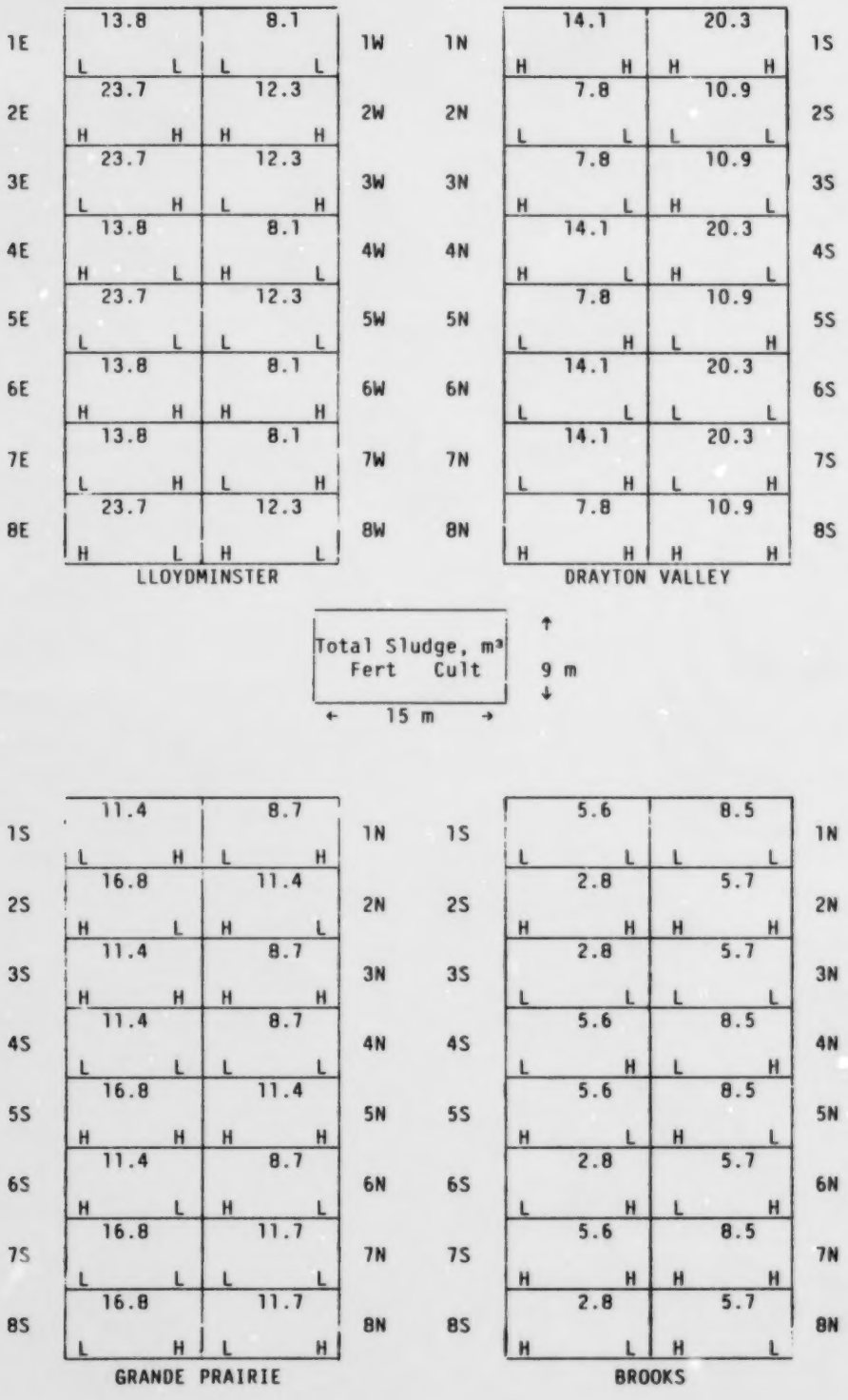

1E 13.8 L L 8.1 L L 1W
2E 23.7 H H 12.3 H H 2W
3E 23.7 L H 12.3 L H 3W
4E 13.8 H L 8.1 H L 4W
5E 23.7 L L 12.3 L L 5W
6E 13.8 H H 8.1 H H 6W
7E 13.8 L H 8.1 L H 7W
8E 23.7 H L 12.3 H L 8W
LLOYDMINSTER
1N 14.1 H H 20.3 H H 1S
2N 7.8 L L 10.9 L L 2S
3N 7.8 H L 10.9 H L 3S
4N 14.1 H L 20.3 H L 4S
5N 7.8 L H 10.9 L H 5S
6N 14.1 L L 20.3 L L 6S
7N 14.1 L H 20.3 L H 7S
8N 7.8 H H 10.9 H H 8S
DRAYTON VALLEY
Total Sludge, m³
Fert Cult
9 m
15 m
1S 11.4 L H 8.7 L H 1N
2S 16.8 H L 11.4 H L 2N
3S 11.4 H H 8.7 H H 3N
4S 11.4 L L 8.7 L L 4N
5S 16.8 H H 11.4 H H 5N
6S 11.4 H L 8.7 H L 6N
7S 16.8 L L 11.7 L L 7N
8S 16.8 L H 11.7 L H 8N
GRANDE PRAIRIE
1S 5.6 L L 8.5 L L 1N
2S 2.8 H H 5.7 H H 2N
3S 2.8 L L 5.7 L L 3N
4S 5.6 L H 8.5 L H 4N
5S 5.6 H L 8.5 H L 5N
6S 2.8 L H 5.7 L H 6N
7S 5.6 H H 8.5 H H 7N
8S 2.8 H L 5.7 H L 8N
BROOKS

Figure 1. Plot arrangement and treatments of oily sludge, fertilizer, and cultivation at the four landtreatment sites, 1982-1985.

detected. Although the pH of the soils declined over 2 years, it remained above 7 and mobilization of metals did not pose a problem. Changes in the physical properties of the soils were caused by salt water and repeated sludge applications could limit the productivity of the land for agriculture.

Many questions remain to be addressed: the rates of degradation of recalcitrant materials, the medium and long-term environmental effects of landtreatment, and the ability to return the land to agricultural production. The results of the research program will provide a scientific basis for the establishment of guidelines for the landtreatment of oil field wastes, will greatly enhance our understanding of landtreatment processes, and will allow the environmental effects of landtreatment to be assessed.

2. OVERALL STUDY OBJECTIVES

Experimental sites in four climatically and environmentally distinct regions of Alberta were monitoried for 4 years previous to the initiation of this phase of the study. Intensive study of all four sites was beyond the scope of this study and thus Lloydminster was selected for the most intensive efforts, followed by Drayton Valley where land farming of oily wastes is being conducted on an operational scale. Following the wishes of the CPA Environmental Research Advisory Council, the sites at Grande Prairie and Brooks were given the lowest priority with only minimal efforts being directed at soil productivity studies and no monitoring of oil degradation, oil residue composition or water quality. Using this partitioning of sites the major objectives of this study were:

1. To determine the effects of landtreatment on soil productivity and the feasibility of returning landtreatment sites to useful crop production.
2. To determine if greenhouse assessments of soil productivity were useful indicators of field productivity.
3. To determine the effects of landtreatment on soil physical and inorganic chemical characteristics and how these related to soil productivity.
4. To further monitor the degradation of oily sludges applied to soils.
5. To chemically characterize the oily sludge residues in soils.
6. To develop a technique for assessing the uptake of aromatic hydrocarbons by plants and to assess the potential danger of the uptake of such compounds in crop utilization.
7. To determine the effects of landtreatment with oily sludges on surface and groundwater quality (hydrocarbon content and inorganic ion contamination).
8. To develop guidelines for landtreatment practices in Alberta which would permit a practical disposal method in an environmentally safe manner.

3. PRODUCTIVITY OF SOILS TREATED WITH OILY SLUDGES

3.1 OBJECTIVES

The major objective of this phase of the study was to assess the possibility of returning landtreatment sites to normal agricultural uses. Specifically, the growth of appropriate crops was determined at each of the four sites and the effects of sludge application rate, fertilization rate and cultivation frequency on crop production was assessed. Plant growth results were compared to the soil inorganic chemistry results and the oil residue content and composition in order to determine the causes of plant growth inhibition.

3.2 MATERIALS AND METHODS

3.2.1 Field assessments of soil productivity

3.2.1.1 Planting of landtreatment field sites. All four landtreatment sites that were initiated in either 1982 (Lloydminster, Drayton Valley, and Grande Prairie) or 1983 (Brooks) were planted in June 1986. The selection of crops and fertilizer levels were determined by local farming practices. Each site was cultivated and planted by a local contractor as reported in Table 1. The entire plot area as well as the surrounding buffer zone was cultivated, fertilized, and planted. The buffer zones were planted to provide control areas free of oily sludges to determine the effect of the 16 sludge-cultivation-fertilization treatments on crop yield.

3.2.1.2 Field assessments of crop growth. The technique for sampling soils and crops followed the system used in previous years to allow comparisons with data of Peake et al. (1984, 1985) and Peake and Connery (1986). To minimize variation, samples were taken from five preselected points in each plot, the points remaining the same from year to year. The Lloydminster site was sampled for plant growth on September 4, 1986. Five 1 m^2 samples (clip plots) were taken adjacent to each oil content sample point (see below) in plots 1W, 4W, 5W, 8W, and the west border control. These represented the treatment

Table 1. Planting of land treatment sites in 1986.

Site[1] (Planting date)	Cultivation	Fertilizer	Seed
Lloydminster (June 9)	Rototilled	27-27-0 80 kg/ha	Bonanza barley 25 kg used
Drayton Valley (June 10)	Harrowing	16-20-0 34-0-0 50 kg/ha each	30% Creeping red fescue 30% Richmond timothy 20% Alsike clover 20% Meadow foxtail 15 kg/ha
Grande Prairie (June 17)	Harrowing	12-15-0 50 kg/ha	10 lb Alfalfa 4 lb Timothy Total used
Brooks (June 18)	Harrowing	11-51-0 34-0-0 50 + 25 kg Total used	40% Crested wheatgrass 40% Russian wild rye 20% Sainfoin 50 kg used

[1] All of site areas at Lloydminster, Grande Prairie, and Brooks, including borders were cultivated and planted. Plots 24,000 ft^2 (2230 m^2), borders approximately 7000 ft^2 (650 m^2). Only the plot area at Drayton Valley was planted.

combinations of high sludge-high fertilizer (8W), high sludge-low fertilizer (5W), low sludge-high fertilizer (4W), low sludge-low fertilizer (1W) on the plots treated with sludge in 1982, 1984 and 1985 and cultivated least frequently. Growth on the other 12 treatments were rated from very poor to excellent by visual examination. Barley was harvested by clipping at the ground line and collecting all the plant material within each quadrant. A total of 25 samples were taken including five from the control area. The control area was the untreated strip on the west side of plots. Areas in the control that contained excessive amounts of weeds or had suffered from excessive moisture were avoided (i.e. nonrandom selection). This was not a true control as it had not been cultivated and fertilized in the 1982-85 period but was intended to provide soil and plant samples uncontaminated with oily sludges.

The Drayton Valley plots were sampled September 16, 1986 for plant production. Four plant species had been planted in the hay mixture and in all plots timothy was the dominant plant; it was in head in all but the poorest plots. Clover and creeping red fescue were also present but the individual plants were small and widely scattered. Weeds were not common except in a few localized areas and they included foxtail barley, thistle, dandelion, marestail, and lamb's quarters. The border of the plot area was not planted and thus, the Drayton Valley site lacked a sludge-free control. A dense cover of clover was present on most of the border area.

The vegetation was sampled in the same manner as the Lloydminster site with five clip-plots per treatment. The soil was rocky which prevented cutting plants closer than 3-5 cm from the soil surface. Plant samples were all washed in the laboratory to remove soil contamination and air dried.

All plant samples from Lloydminster and Drayton Valley were air dried and stored until they could be processed. The grain was separated from the barley straw by hand and straw and grain weighed separately. Subsamples were dried at 80°C to obtain oven dry weights. Hay from Drayton Valley was also weighed after air drying. The entire samples of barley straw and hay were ground in a hammer mill to facilitate subsampling for chemical analyses.

In addition to the quantitative plant sampling at Lloydminster and Drayton Valley, plant growth on all treatments at all four sites was assessed by visual estimates. Although somewhat subjective, this was intended to provide information on gross effects and to serve as a guide for future sampling. Overall plant growth in each plot was rated as very poor, poor, fair, good or excellent. Estimates were made at Grande Prairie on September 23, 1986 and at Brooks on October 8, 1986.

3.2.1.3 Soil sampling. Soil samples were taken at each site at the same time as plant growth was assessed. The pattern for soil sampling was the same as was done in previous years, i.e. a systematic selection of five points per plot (Peake et al. 1985). At Lloydminster soil

samples were taken from all 16 plots for oil content, in four plots plus the control for soil chemical analysis and two plots plus the control for greenhouse studies. For oil content, five cores were taken at each of the five preselected points per plot and the cores combined for each sample point for a total of 80 composite samples (16 treatments x 5 replications). Each core (3 cm diameter) was taken to a depth of approximately 15 cm (rototilling depth).

For nutrient analysis, soil samples were taken from the top 15 cm with a shovel in each clip plot for a total of 25 samples. Additional soil was removed from clip plots 1W, 4W and the control for the greenhouse plant growth study.

At Drayton Valley only the plots sampled for plant growth were sampled for oil content. The soil samples for oil content were not collected by coring as done previously due to the very wet and sticky nature of the surface soil. Soil samples were taken with a shovel from 4 or 5 points in the centre of each clip plot to a depth of about 10 cm. The four treatments with the 1982 and 1984 sludge applications and low cultivation rate were sampled for oil content and soil properties. Soils for the greenhouse study were taken from 2N (low sludge and low fertilization), 3N (low sludge and high fertilization), 6N (high sludge and low fertilization), and the border (control) area. Plant growth on these plots ranged from good to poor. Most of the control area (northeast end) supported a dense growth of clover.

At Grande Prairie soil samples for the greenhouse study were taken from five points per plot from plots 4N (low sludge, fertilizer and cultivation), 6N (low sludge, high fertilizer and low cultivation) and the northern border area control. At Brooks soil samples (approximately 4 - 5 kg, five replicates) were taken from three plots and the southern (control) area for the greenhouse growth study. Samples were removed from plot 3S (low sludge, low fertilizer and cultivation), 8S (low sludge, high fertilizer, low cultivation) and 1N (high sludge 1983 and 1984, and low fertilization and cultivation). The latter treatment was included as it was the most extreme in terms of sludge level, yet seedlings had become established in the fall although they were very small.

3.2.1.4 Soil physical and chemical analysis. Soils from Lloydminster and Drayton Valley sampled for oil content were sieved through a 2 mm sieve prior to analysis. Soil for inorganic analyses and greenhouse studies was sieved in the moist condition through a 4 mm sieve, thoroughly mixed and subsampled. Physical and chemical analyses were done by the Earth Sciences Division, Alberta Environment,Lethbridge, Alberta. Available N and P were estimated by extraction of NO_3-N with 0.01 N $CuSO_4$ + 0.007N Ag_2SO_4, NH_4-N with 2N KCl and P with 0.03 N H_2SO_4 + 0.03 N NH_4F. Electrical conductivity and pH were measured in a saturated paste, soluble salts in a 5/1 (V/W) solution/soil ratio.

3.2.1.5 Plant nutrient and heavy metal analysis. The ground plant samples (barley straw and timothy hay) were subsampled and digested for analysis. The subsamples (0.25 g) were digested in 5 mL H_2SO_4 and 4 mL H_2O_2 and diluted to 75 mL. The final acid concentration was 6.67%. Total N and P were determined with a Technicon apparatus. The acid digests were submitted to the Earth Sciences Division, Lethbridge for K, Mg and Ca analyses. Two samples, Lloydminster 1W and 4W were submitted for heavy metal analyses (Fe, Cu, ZN, Pb, Mn, Cd and Ni).

3.2.2 Greenhouse assessments of soil productivity

Soil sieved through a 4 mm screen from each landtreatment site was used to determine the effects of oily sludge application on plant growth under controlled conditions. The soil was taken from the field clip plots with the exception of the Drayton Valley control (not planted in the field) and Brooks plot 1N which presented the extreme case at that site. Five replicate samples were used for each of the 14 field treatments and each sample was planted with Rambler alfalfa and Diamond variety barley (5 replicates x 14 treatments x 2 species = 140 pots). The soil was placed in 5 inch standard pots with a layer of cheesecloth in the bottom to prevent soil from leaking out. Ten seeds of either alfalfa or barley were planted in each pot October 30, 1986 and the pots were placed in a greenhouse without supplemental lighting. Fertilizer was applied 13 days after planting at rates

equivalent to those used in the field (71 mg NH_4NO_3 and 5 mg 0-20-0 per pot) after dissolving in water. These rates were equivalent to 25 kg $N \cdot ha^{-1}$ and 5 kg $P \cdot ha^{-1}$.

Germination and emergence was measured 13 days after planting. The barley initially grew rapidly but after several weeks growth rates decreased and thrips infested both the alfalfa and barley. In order to save the experiment, insecticides and fertilizer were applied and light increased. The plants were sprayed weekly with a variety of insecticides in attempts to control the thrips , but damage continued to be a problem throughout the experiment. After 40 days two 400 W high pressure sodium lamps were installed and the day length increased to 14 h with an intensity of about 100-150 $\mu E \ m^{-2} \cdot sec^{-1}$ (30-40 klx). A second fertilizer application at twice the previous rate was also made at this time. As a result of these modifications plant growth improved substantially and the barley was harvested when 54 days old and the alfalfa when 76 days old. Watering was done by hand for the first 56 days and by daily automatic watering from 56 to 76 days. Plants were harvested by clipping off the shoots, which were dried at 80°C and weighed. No measurements were made on soil characteristics.

3.3 RESULTS

3.3.1 Crop growth

3.3.1.1 Visual estimates of growth at Lloydminster. The growth of barley ranged from very poor to excellent in the sludge treated plots (Table 2, Figures 2 and 3). Unexpectedly, growth was not entirely related to the experimental treatments. Growth was very similar on both plots 1W and 1E although nearly twice as much sludge had been applied to plot 1E as to 1W. Growth was excellent in plot 8W which had received the high sludge treatment in 1982 but growth in other high sludge treatments was poor or very poor. Neither fertilizer nor cultivation appeared to have influenced barley growth. Grain production was

Table 2. Visual estimates of plant vigor and growth of Bonanza barley on the Lloydminster site (September 4, 1986).

Plot	Sludge Application (year and m^3)		Fertilizer	Cultivation	Plant Growth
1W[1,2]	82,84,85	4.2 + 1.6 + 2.3	Low	Low	Good
1E	82,83,84,85	4.2 + 5.7 + 1.6 + 2.3	Low	Low	Good
2W	82,84,85	8.4 + 1.6 + 2.3	High	High	Very Poor
2E	82,83,84,85	8.4 + 11.4 + 1.6 + 2.3	High	High	Poor
3W	82,84,85	8.4 + 1.6 + 2.3	Low	High	Poor
3E	82,83,84,85	8.4 + 11.4 + 1.6 + 2.3	Low	High	Poor
4W[1,2]	82,84,85	4.2 + 1.6 + 2.3	High	Low	Fair
4E	82,83,84,85	4.2 + 5.7 + 1.6 + 2.3	High	Low	Poor
5W[1]	82,84,85	8.4 + 1.6 + 2.3	Low	Low	Poor
5E	82,83,84,85	8.4 + 11.4 + 1.6 + 2.3	Low	Low	Poor
6W	82,84,85	4.2 + 1.6 + 2.3	High	High	Fair
6E	82,83,84,85	4.2 + 5.7 + 1.6 + 2.3	High	High	Very Poor
7W	82,84.85	4.2 + 1.6 + 2.3	Low	High	Fair
7E	82,83,84,85	4.2 + 5.7 + 1.6 + 2.3	Low	High	Poor
8W[1]	82,84,85	8.4 + 1.6 + 2.3	High	Low	Excellent
8E	82,83,84,85	8.4 + 11.4 + 1.6 + 2.3	High	Low	Poor
Control[1]	None[3]	-	None	None	Good

[1] Plots sampled for plant growth and soil properties.

[2] Plots sampled for greenhouse study.

[3] Soil analysis showed that the border was contaminated with oil and contained 1.3% hydrocarbons.

Figure 2. Barley in Lloydminster plot 1W in foreground and 1E in background September 4, 1986.

Figure 3. Barley in Lloydminster plot 5W in foreground and 5E in background September 4, 1986. Surface water runoff pond directly in front of gate.

good in plots 1W, 1E, and 8W but scant or absent in the other plots. Growth and grain production in plots 1W, 1E, and 8W was as good or better than in the control area (the control area contained oil contaminants, see Section 4.2.3.3). The roots of barley plants that were growing poorly were stunted and only appeared to penetrate the surface few centimeters of soil.

Drainage and moisture conditions appeared to have a major influence on barley growth. Plots 1 and 8 were at the high points of the experimental area with plots 4 and 5 in the lowest positions. Where there was evidence of past standing water growth was always poor, including in the western control strip.

3.3.1.2 Visual estimates of growth at Drayton Valley. The growth of timothy was good in all plots containing the lowest levels of sludge (1982 applications) (Table 3, Figures 4 and 5). Growth in low application rate plots in which sludge was also applied in 1983 ranged from fair to good and appeared to be affected by fertilizer rate. In the high application rate plots in which sludge had been added in 1982 growth ranged from poor to fair. The best growth appeared to be in those plots which had received high fertilizer applications. The growth of timothy in plots treated with high rates of sludge for 2 years was poor to very poor. Growth appeared to be somewhat better in the plots fertilized the most heavily.

3.3.1.3 Visual estimates of growth at Grande Prairie. All plots and the border had been planted with a mixture of alfalfa and timothy. Plant growth on all plots was poor to very poor (Table 4, Figure 6 and 7). Both alfalfa and timothy were present but the plants were scattered and small, generally being less than 5 cm tall. In the treatments receiving the highest levels of sludge, the plants were chlorotic and had apparently stopped growing soon after emergence. Growth in the control (border) areas was fair to poor with plants not exceeding 15 cm in height. Insufficient plant material was present to permit quantitative sampling. Growth of weeds, especially dandelions, was good in the strips between plots. Growth of alfalfa in the adjacent agricultural field was good.

Table 3. Visual estimates of plant vigor and growth of hay mixture (primarily timothy) on the Drayton Valley site (September 16, 1986).

Plot	Sludge Application (year and m³)		Fertilizer	Cultivation	Plant Growth
1N	82	12.5	High	High	Fair
1S	82,83	12.5 + 6.2	High	High	Poor
2N[1,2]	82	6.2	Low	Low	Good
2S	82,83	6.2 + 3.1	Low	Low	Good
3N[1,2]	82,84	6.2	High	Low	Good
3S	82,83	6.2 + 3.1	High	Low	Good
4N[1]	82	12.5	High	Low	Fair
4S	82,83	12.5 + 6.2	High	Low	Poor
5N	82	6.2	Low	High	Good
5S	82,83	6.2 + 3.1	Low	High	Good
6N[1,2]	82	12.5	Low	Low	Poor
6S	82,83	12.5 + 6.2	Low	Low	Very Poor
7N	82	12.5	Low	High	Fair
7S	82,83	12.5 + 6.2	Low	High	Very Poor
8N	82	6.2	High	High	Good
8S	82,83	6.2 + 3.1	High	High	Fair

[1] Plots sampled for plant growth and soil properties.

[2] Plots sampled for the greenhouse study (unplanted border also sampled).

Figure 4. Timothy hay in Drayton Valley plot 3N in foreground and 3S down slope September 16, 1986.

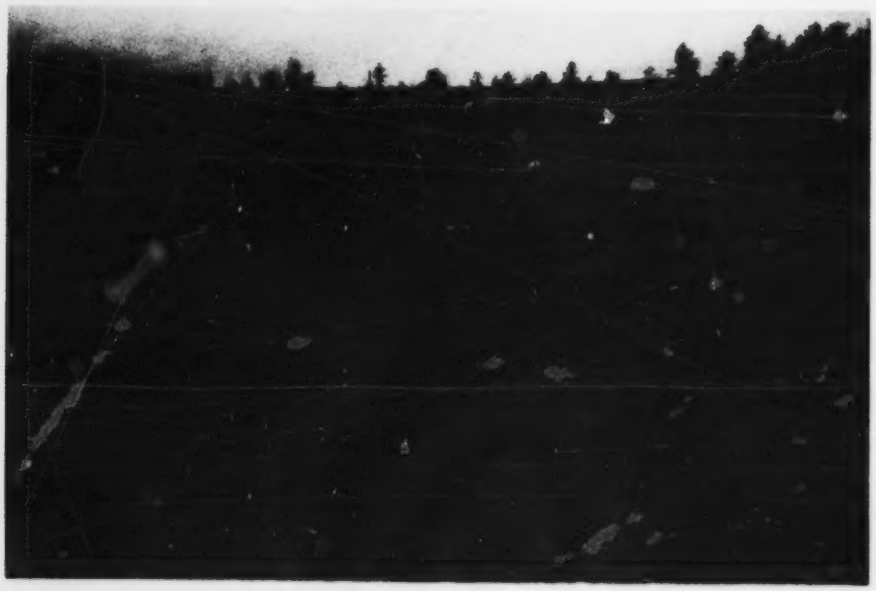


Figure 5. Timothy hay in Drayton Valley plot 6N in foreground and 6S down slope September 16, 1986.

Table 4. Visual estimates of plant vigor and growth of alfalfa and timothy on the Grande Prairie site (1986 September 23).

Plot	Sludge Application (year and m^3)		Fertilizer	Cultivation	Plant Growth
1N	82,84	2.7 + 6	Low	High	Poor
1S	82,83,84	2.7 + 2.7 + 6	Low	High	Poor
2N	82,84	5.4 + 6	High	Low	Very Poor
2S	82,83,84	5.4 + 5.4 + 6	High	Low	Very Poor
3N	82,84	2.7 + 6	High	High	Very Poor
3S	82,83,84	2.7 + 2.7 + 6	High	High	Very Poor
4N[1]	82,84	2.7 + 6	Low	Low	Poor
4S	82,83,84	2.7 + 2.7 + 6	Low	Low	Poor
5N	82,84	5.4 + 6	High	High	Very Poor
5S	82,83,84	5.4 + 5.4 + 6	High	High	Very Poor
6N[1]	82,84	2.7 + 6	High	Low	Poor
6S	82,83,84	2.7 + 2.7 + 6	High	Low	Poor
7N	82,84	5.4 + 6	Low	Low	Poor
7S	82,83,84	5.4 + 5.4 + 6	Low	Low	Very Poor
8N	82,84	5.4 + 6	Low	High	Poor
8S	82,83,84	5.4 + 5.4 + 6	Low	High	Very Poor
Control[1]	None		None	None	Fair

[1] Soil sampled for greenhouse assessments.

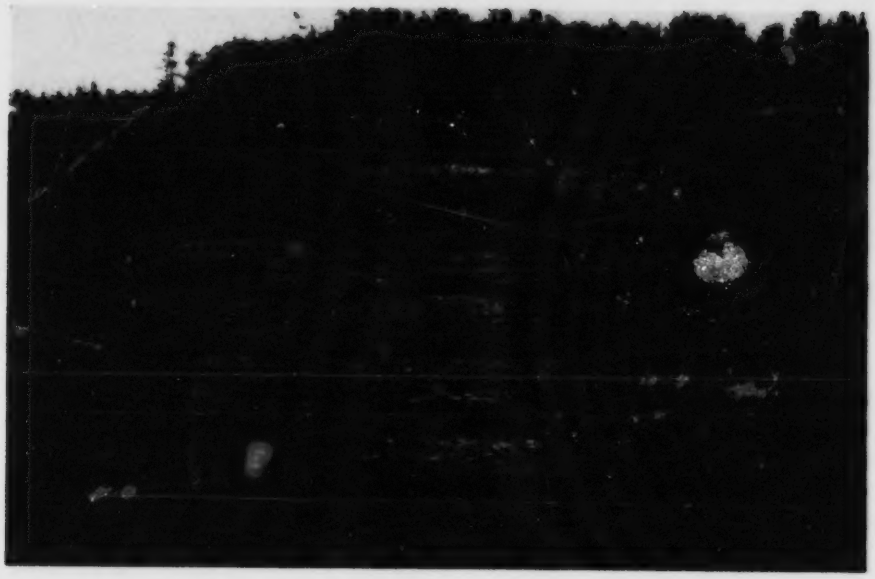


Figure 6. Alfalfa and timothy at Grande Prairie in plots 4N in foreground and 4S in background September 23, 1986.

Figure 7. Alfalfa and timothy at Grande Prairie in plot 6N in foreground and 6S in background September 23, 1986.

3.3.1.4 Visual estimates of growth at Brooks. The northern plots which had received sludge in both 1983 and 1984 appeared to be almost barren with the exception of plot 3N in which a few clumps of grass were up to 15 cm tall (Table 5). However, upon closer inspection, very young grass and sainfoin were present in all the northern plots. It appeared that seed had germinated under the moist fall conditions. The grass was 3 to 5 cm tall with roots about 3 cm long. The sainfoin usually was very small with only one pair of true leaves. It is not known whether seed also germinated in the early summer and subsequently died or that no germination occurred on the northern plots in June. It is also not known whether the plants that became established will continue to grow as the roots extend deeper into the sludge-containing soil.

Growth in the plots treated only in 1983 was obviously better than in the northern plots treated in both 1983 and 1984 (Figure 8 and 9). However, establishment was very patchy, often in single rows and largely consisted of one grass species. It appeared that the microenvironmental moisture condition was a critical factor in success regardless of sludge treatment. Plants in the southern plots were of similar size to those in the adjacent untreated border. The best coverage was in plots 2S and 3S which received the low level of sludge. The very patchy establishment (overall coverage 5-10%) made precise estimates difficult. However, as there was germination in all areas in the fall, treatment effects may be more apparent in the second growing season.

Establishment and growth in the border (control) was also very patchy with only the south border supporting a reasonable crop cover. Other border areas were densely populated with weeds, primarily kochia and Russian thistle. The areas around all marker posts in the plots were also densely overgrown with Russian thistle and kochia which reached heights of 0.5 to 1 m. Weeds were uncommon in the plots themselves but may become a problem in the future.

3.3.1.5 Quantitative estimates of crop growth at Lloydminster and Drayton Valley. The best growth of barley at Lloydminster occurred on the plot receiving a high level of sludge in 1982, with production of

Table 5. Visual estimates of plant vigor and growth of dryland pasture species on the Brooks land treatment site (October 8, 1986).

Plot	Sludge Application (year and m^3)		Fertilizer	Cultivation	Plant Growth
1S	83	5.6	Low	Low	Poor
1N[1]	83, 84	5.6 + 2.9	Low	Low	Extremely poor
2S	83	2.8	High	High	Fair
2N	83, 84	2.8 + 2.9	High	High	Extremely poor
3S[1]	83	2.8	Low	Low	Fair
3N	83, 84	2.8 + 2.9	Low	Low	Very poor
4S	83	5.6	Low	High	Poor
4N	83, 84	5.6 + 2.9	Low	High	Extremely poor
5S	83	5.6	High	Low	Poor
5N	83, 84	5.6 + 2.9	High	Low	Extremely poor
6S	83	2.8	Low	High	Poor
6N	83, 84	2.8 + 2.9	Low	High	Extremely poor
7S	83	5.6	High	High	Very poor
7N	83, 84	5.6 + 2.9	High	High	Extremely poor
8S[1]	83	2.8	High	Low	Poor
8N	83, 84	2.8 + 2.9	High	Low	Extremely poor
Control[1]	None		None	None	Fair

[1] Soil sampled for greenhouse assessments.

Figure 8. Dryland pasture grass at Brooks in plot 3S in foreground and 3N in background October 8, 1986.

Figure 9. Dryland pasture grass at Brooks in plot 8S in foreground and 8N in background October 8, 1986.

grain and straw equalling production on the control area (Table 6). However, on plot 5W which received the same amount of sludge, growth was extremely poor. On the two plots sampled which received the low levels of sludge, growth was much less than in the 8W plot or the control. In general grain accounted for about one-half of the shoot production.

At Drayton Valley timothy grew well in plots receiving both high and low levels of sludge in 1982 (Table 7). However, where low levels of fertilizer were applied (plot 6N), growth was depressed.

3.3.2 Crop nutrient and heavy metal contents

The N content of the barley straw was lowest in the most productive plots (Table 8). Individual plants in plots 4W and 5W which contained high levels of N were very small. The lowest concentration of P occurred in plants grown in the most productive plot (8W) and the highest in plants from the least productive plot (5W). At Drayton Valley there were little differences in N and P concentrations among the four treatments (Table 9). Concentrations of K, Ca and Mg all were within the normal range except K levels were low in straw grown on Lloydminster plots 4W and 5W. Concentrations of heavy metals did not appear to be excessive; however, background levels in the reagents were high for Pb and Ni which prevented the detection of actual concentrations (Table 10).

3 3.3 Soil Analyses

Neither sludge nor past fertilizer treatments appeared to substantially affect total or available soil N or available P at Lloydminster (Table 11). Total N was lowest in the control area but available N was low in all areas. Soil pH was close to neutrality in all plots and the addition of oily sludges did not affect the soil moisture holding capacity (Table 12). Electrical conductivity (E.C.) and the sodium absorption ratio (SAR) was lowest in plot 8W which supported the best growth of barley. The electrical conductivity was highest in plots 4W and 5W in which barley grew poorly. Treatment with oily sludges increased total C from 1.7 to 2.5%. The concentrations of

Table 6. Primary production of Bonanza barley grown on oily sludge treated soils at Lloydminster.

Plot	Sludge application m^3/plot (1982/84/85)	Fertilizer[1]	Biomass ODW, $g \cdot m^{-2}$ ± SD Grain	Straw
1W	4.2 + 1.6 + 2.3	Low	83 ± 32	88 ± 36
4W	4.2 + 1.6 + 2.3	High	17 ± 13	21 ± 13
5W	8.4 + 1.6 + 2.3	Low	1 ± 1	3 ± 3
8W	8.4 + 1.6 + 2.3	High	174 ± 108	188 ± 135
Control[2]	0	0	194 ± 37	222 ± 50

[1] See Peake et al. (1985) and Peake and Connery (1986).

[2] Control area soil was contaminated with oil residues.

Table 7. Primary production of a timothy-alfalfa hay grown on oily sludge treated soils at Drayton Valley.

Plot	Sludge application m^3/plot (1982)	Fertilizer[1]	Biomass ODW, $g \cdot m^{-2}$ ± SD
2N	6.2	Low	147 ± 60
3N	6.2	High	136 ± 74
6N	12.5	Low	56 ± 34
4N	12.5	High	146 ± 116

[1] See Peake et al. (1985).

Table 8. Nutrient concentrations in barley straw grown in oily sludge treated soils at Lloydminster.

Plot	Sludge[1]	Fert[2]	N	P	K	Ca	Mg
			% ($\bar{x}$ ± SD)				
1W	Low	Low	1.12 ± 0.32	0.15 ± 0.02	0.89 ± 0.14	0.20 ± 0.02	0.10 ± 0.01
4W	Low	High	1.30 ± 0.29	0.16 ± 0.05	0.57 ± 0.07	0.31 ± 0.02	0.12 ± 0.01
5W	High	Low	1.60 ± 0.40	0.30 ± 0.12	0.27 ± 0.08	0.38 ± 0.10	0.15 ± 0.01
8W	High	High	1.04 ± 0.22	0.10 ± 0.01	0.98 ± 0.20	0.22 ± 0.01	0.12 ± 0.02
Control	None	None	0.98 ± 0.24	0.17 ± 0.02	0.74 ± 0.06	0.21 ± 0.01	0.11 ± 0.01

[1] Low application = 4.2 + 1.6 + 2.3 m^3 per plot (135 m^2) in 1982, 1984 and 1985 respectively. High application the same except 8.4 m^3 applied in 1982.

[2] See Peake et al. (1985) and Peake and Connery (1986).

Table 9. Nutrient concentrations in a timothy-alfalfa hay grown in oily sludge treated soils at Drayton Valley.

Plot	Sludge[1]	Fert[2]	N	P	K	Ca	Mg
			% ($\bar{x}$ ± SD)				
2N	Low	Low	1.84 ± 0.22	0.15 ± 0.01	1.40 ± 0.10	0.16 ± 0.02	0.09 ± 0.01
3N	Low	High	1.74 ± 0.20	0.17 ± 0.02	1.47 ± 0.11	0.16 ± 0.02	0.10 ± 0.01
6N	High	Low	1.80 ± 0.37	0.16 ± 0.02	1.40 ± 0.12	0.17 ± 0.01	0.10 ± 0.01
4N	High	High	1.72 ± 0.15	0.15 ± 0.01	1.36 ± 0.16	0.25 ± 0.08	0.16 ± 0.06

1 Low application = 6.2 + 1.6 m^3 per plot (135 m^2) in 1982 and 1984 respectively. High application the same except 12.5 m^3 applied in 1982.

2 See Peake et al. (1985).

Table 10. Heavy metal content ($\mu g \cdot g^{-1}$) of barley straw grown on Lloydminster soil treated with oily sludges.

Element	Lloydminster Plot	
	Control	4W
Fe	59 ± 24	118 ± 60
Cu[1]	<2	<2
Zn[1]	<20	<20
Pb[1]	<180	<180
Mn	28 ± 6	56 ± 12
Cd[1]	<20	<20
Ni[1]	<60	<60

1 Measurements identical to or less than reagent blank.

Table 11. Nitrogen and phosphorous status of soils treated with oily sludges at Lloydminster.

Plot	Sludge[1]	Fert[2]	Total N % ($\bar{x}$ ± SD)	NO_3-N $mg \cdot kg^{-1}$ ($\bar{x}$ ± SD)	NH_4-N $mg \cdot kg^{-1}$ ($\bar{x}$ ± SD)	P $mg \cdot kg^{-1}$ ($\bar{x}$ ± SD)
1W	Low	Low	0.25 ± .01	4.7 ± 2.7	2.1 ± 0	6.4 ± 1.4
4W	Low	High	0.21 ± .01	1.4 ± 1.2	1.8 ± 0	10.0 ± 2.0
5W	High	Low	0.20 ± .01	<0.4	1.4 ± 0.3	5.8 ± 0.9
8W	High	High	0.25 ± .02	0.5 ± 0.3	2.6 ± 1.0	9.1 ± 1.3
Control	None	None	0.17 ± .02	0.7 ± 0.6	2.1 ± 0.3	8.6 ± 2.4

1 Low application = 4.2 + 1.6 + 2.3 m^3 per plot (135 m^2) in 1982, 1984 and 1985 respectively. High application the same except 8.4 m^3 applied in 1982.

2 See Peake et al. (1985) and Peake and Connery (1986)

Table 12. Chemical and moisture characteristics of soils treated with oily sludges at Lloydminster.

Plot	Sludge[1]	Fert[2]	pH	E.C. ($ds \cdot m^{-1}$)	SAR	Total C (%)	$CaCO_3$ (%)	Moisture 1/3 bar (%)
			($\bar{x} \pm SD$)					
1W	Low	Low	7.1 ± 0.2	2.9 ± 0.7	6.2 ± 1.2	5.1 ± 0.3	3.0 ± 1.0	20.6 ± 0.6
4W	Low	High	6.8 ± 0.1	4.8 ± 1.6	6.0 ± 1.0	5.0 ± 0.5	0.2 ± 0.2	19.1 ± 0.6
5W	High	Low	6.9 ± 0.2	4.2 ± 1.5	5.3 ± 1.0	5.8 ± 0.5	0.6 ± 0.2	17.6 ± 0.7
8W	High	High	7.2 ± 0.1	1.3 ± 0.1	2.6 ± 0.3	5.2 ± 0.5	1.0 ± 0.7	20.6 ± 2.0
Control	None	None	7.1 ± 0.2	2.6 ± 0.4	3.6 ± 1.0	3.3 ± 0.2	2.1 ± 1.6	20.7 ± 0.9

[1] Low application = 4.2 + 1.6 + 2.3 m^3 per plot (135 m^2) in 1982, 1984 and 1985 respectively. High application the same except 8.4 m^3 applied in 1982.

[2] See Peake et al. (1985) and Peake and Connery (1986).

Ca, Mg, Na, K, Cl and SO_4 were all lowest in plot 8W and highest in 4W and 5W (Table 13, Appendix Table 1). The rates of sludge and fertilizer applications did not appear to be directly related to the saturated extract ionic composition (i.e., water soluble salts).

Total soil N levels at Drayton Valley were similar to those at Lloydminster and appeared to be somewhat higher in the sludge treated soils (Table 14). Both available N and P were low in both the treated and untreated soils. The pH of the soils was close to neutrality and the sludge did not appear to affect the moisture holding capacity or sodium absorption ratio (Table 15). Sludge additions resulted in slightly higher electrical conductivity and substantial increases in $CaCO_3$ content and total C. Total C was 2.7 to 4.9% greater in the sludge treated soils than in the control area (2.8%).

Concentrations of ions in the saturated extracts were generally lower at Drayton Valley than at Lloydminster (Table 16).
Sludge additions had little effect on solution ionic composition other than to slightly increase K and substantially increase SO_4.

3.3.4 Greenhouse productivity assessment

The germination and emergence of barley exceeded 86% in all 14 treatments (Table 17). The germination of alfalfa was less than that of barley but still ranged from 58 to 82%. Germination of alfalfa was slightly less in sludge treated soils from Lloydminster, Drayton Valley and Grande Prairie than in sludge-free soils but varied little among sludge treatments.

Growth of both barley and alfalfa was negatively influenced by the initially poor light conditions and foliage damage by thrips but sufficient growth occurred to provide a comparison with field results. In contrast to the field results where Bonanza variety barley was used, growth of Diamond variety barley and alfalfa occurred in all the treatments tested in the greenhouse (Table 18). Barley grew much better than the legume but did not reflect the field data except in extreme cases. Sludge depressed barley growth in the two Lloydminster soils equally (50%) in the greenhouse whereas in the field, growth in 1W was depressed 60% and in 4W, 90%. The pattern in Drayton Valley greenhouse

Table 13. Cation and anion concentrations in saturated extracts of soils treated with oily sludges at Lloydminster

Plot	Sludge[1]	Fert[2]	Ca	Mg	Na	K	NH_4-N	NO_3-N	Cl	SO_4	HCO_3
			m.e. L^{-1} ($\bar{x} \pm SD$)								
1W	Low	Low	10.7 ± 2.0	3.6 ± 0.9	16.5 ± 4.4	0.19 ± .01	0.07 ± .01	0.02 ± .01	16.3 ± 5.2	6.9 ± 2.0	5.8 ± .5
4W	Low	High	21.8 ± 6.9	7.2 ± 2.4	23.0 ± 7.0	0.24 ± .05	0.07 ± .01	0.02 ± .01	32.5 ± 13.8	11.3 ± 3.7	5.3 ± .2
5W	High	Low	19.8 ± 5.9	6.9 ± 2.6	19.8 ± 6.7	0.18 ± .06	0.06 ± .01	0.05 ± .04	25.3 ± 14.6	11.9 ± 1.8	6.2 ± .5
8W	High	High	7.8 ± 0.9	1.9 ± 0.5	5.6 ± 0.5	0.10 ± .01	0.06 ± .003	0.01 ± .003	3.3 ± 1.2	5.1 ± 1.1	5.2 ± .4
Control	None	None	11.9 ± 2.9	4.6 ± 1.0	10.0 ± 2.1	0.18 ± .02	0.05 ± .01	0.02 ± 0	16.7 ± 2.9	5.3 ± 1.3	4.0 ± .5

[1] Application = 4.2 + 1.6 + 2.3 m^3 per plot (135 m^2) in 1982, 1984, and 1985, respectively. High application the same except 8.4 m^3 applied in 1982.

[2] See Peake et al. (1985) and Peake and Connery (1986).

Table 14. Nitrogen and phosphorous status of soils treated with oily sludges at Drayton Valley.

Plot	Sludge[1]	Fert[2]	Total N % ($\bar{x}$ ± SD)	NO_3-N $mg \cdot kg^{-1}$ ($\bar{x}$ ± SD)	NH_4-N $mg \cdot kg^{-1}$ ($\bar{x}$ ± SD)	P $mg \cdot kg^{-1}$ ($\bar{x}$ ± SD)
2N	Low	Low	0.21 ± .02	2.0 ± 2.5	2.0 ± 0.3	1.6 ± 0.7
3N	Low	High	0.27 ± .04	9.1 ± 17.3	2.6 ± 0.5	2.0 ± 1.1
6N	High	Low	0.26 ± .01	1.9 ± 2.5	3.3 ± 0.9	0.5 ± 0.1
4N	High	High	0.26 ± .01	3.9 ± 2.0	2.4 ± 0.2	1.1 ± 0.3
Control	None	None	0.18 ± .07	9.5 ± 7.5	3.7 ± 1.8	2.7 ± 1.4

[1] Low application = 6.2 m^3 per plot (135 m^2) in 1982. High application the same except 12.5 m^3 applied in 1982.

[2] See Peake et al. (1985).

Table 15. Chemical and moisture characteristics of soils treated with oily sludges at Drayton Valley.

Plot	Sludge[1]	Fert[2]	pH	E.C ($ds \cdot m^{-1}$)	SAR	Total C (%)	$CaCO_3$ (%)	Moisture 1/3 bar (%)
			($\bar{x} \pm SD$)					
2N	Low	Low	7.3 ± 0.1	0.8 ± 0.1	0.2 ± 0	5.5 ± 0.6	8.5 ± 3.1	28.6 ± 1.4
3N	Low	High	7.2 ± 0.1	0.9 ± 0.2	0.1 ± 0.1	6.9 ± 1.1	8.4 ± 2.6	30.6 ± 2.7
6N	High	Low	7.2 ± 0.2	1.3 ± 0.1	0.2 ± 0.1	7.7 ± 0.6	9.0 ± 1.9	26.9 ± 0.8
4N	High	High	7.3 ± 0.1	0.8 ± 0.1	0.2 ± 0.1	6.9 ± 0.5	7.0 ± 1.6	30.0 ± 1.1
Control	None	None	6.8 ± 0.3	0.5 ± 0.1	0.2 ± 0.1	2.8 ± 1.1	0.3 ± 0.4	31.2 ± 3.1

[1] Low application = 6.2 + 1.6 m^3 per plot (135 m^2) in 1982 and 1984 respectively. High application the same except 12.5 m^3 applied in 1982.

[2] See Peake et al. (1985).

Table 16. Cation and anion concentrations in saturated extracts of soils treated with oily sludges at Drayton Valley.

Plot	Sludge[1]	Fert[2]	Ca	Mg	Na	K	NH_4-N	NO_3-N	Cl	SO_4	HCO_3
			m.e. L^{-1} ($\bar{x} \pm SD$)								
2N	Low	Low	7.5 ± 0.7	1.6 ± 0.2	0.4 ± .1	0.33 ± .01	0.04 ± .01	0.01 ± 0.01	0.35 ± .07	3.5 ± 0.5	4.9 ± .1
3N	Low	High	9.3 ± 1.2	1.8 ± 0.2	0.3 ± .1	0.38 ± .10	0.05 ± .01	0.62 ± 1.36	0.48 ± .13	4.9 ± 1.4	4.9 ± .3
6N	High	Low	12.8 ± 1.2	3.1 ± 0.4	0.7 ± .1	0.61 ± .13	0.07 ± .04	0.02 ± 0.03	0.88 ± .18	8.4 ± 1.1	5.8 ± .3
4N	High	High	7.5 ± 0.5	1.5 ± 0.3	0.3 ± .1	0.42 ± .08	0.06 ± .01	0.03 ± 0.04	0.37 ± .12	2.8 ± 0.40	5.1 ± .1
Control	None	None	4.6 ± 0.9	1.3 ± 0.1	0.3 ± .1	0.21 ± .07	0.12 ± .06	0.03 ± 0.02	0.58 ± .26	0.41 ±0.16	4.5 ± .8

[1] Low application = 6.2 + 1.6 m^3 per plot (135 m^2) in 1982 and 1984, respectively. High application the same except 12.5 m^3 applied in 1982.

[2] See Peake et al. (1985).

Table 17. Germination and emergence of Diamond barley and Rambler alfalfa grown in the greenhouse on soils previously treated with oily sludges in the field.

Site	Field Treatment				Germination	
	Plot	Sludge	Fert[7]	Crop Growth[8]	Barley % ± SD	Alfalfa % ± SD
Lloydminster	1W	Low[1]	Low	Good	90 ± 22	64 ± 13
	4W	Low	High	Fair	92 ± 13	62 ± 13
	C	None	None	Good	98 ± 4	76 ± 5
Drayton Valley	2N	Low[2]	Low	Good	94 ± 9	74 ± 17
	3N	Low	High	Good	100 ± 0	64 ± 11
	6N	High[3]	Low	Poor	100 ± 0	66 ± 9
	C	None	None	NA[9]	98 ± 4	82 ± 15
Grande Prairie	4N	Low[4]	Low	Poor	92 ± 4	74 ± 14
	6N	Low	High	Poor	100 ± 0	74 ± 24
	C	None	None	Fair	100 ± 0	78 ± 23
Brooks	1N	V.High[5]	Low	V.Poor	86 ± 11	60 ± 14
	3S	Low[6]	Low	Fair	100 ± 0	74 ± 19
	8S	Low	High	Poor	100 ± 0	60 ± 17
	C	None	None	Fair	98 ± 4	58 ± 13

1 Application = 4.2 + 1.6 + 2.3 m^3 per plot (135 m^2) in 1982, 1984, and 1985, respectively.
2 Application = 6.2 m^3 per plot (135 m^2) in 1982.
3 Application = 12.5 m^3 per plot (135 m^2) in 1982.
4 Application = 2.7 + 6.0 m^3 per plot (135 m^2) in 1982 and 1984, respectively.
5 Application = 5.6 + 2.9 m^3 per plot (135 m^2) in 1983 and 1984, respectively.
6 Application = 2.8 m^3 per plot (135 m^2) in 1983.
7 See Peake et al. (1985) and Peake and Connery (1986).
8 Based on visual field estimates.
9 NA = not applicable as control area not planted.

Table 18. Yield of Diamond barley and Rambler alfalfa grown in the green- house on soils previously treated with oily sludges in the field.

Site	Field Treatment				Barley	Alfalfa
	Plot	Sludge	Fert[7]	Crop Growth[8]	Dry weight yield $g \cdot pot^{-1} \pm SD$	
Lloydminster	1W	Low[1]	Low	Good	0.74 ± 0.30	0.28 ± 0.26
	4W	Low	High	Fair	0.74 ± 0.26	0.08 ± 0.07
	C	None	None	Good	1.43 ± 0.32	0.44 ± 0.38
Drayton Valley	2N	Low[2]	Low	Good	1.62 ± 0.29	0.35 ± 0.24
	3N	Low	High	Good	1.58 ± 0.32	0.59 ± 0.21
	6N	High[3]	Low	Poor	1.16 ± 0.30	0.29 ± 0.10
	C	None	None	NA[9]	1.94 ± 0.23	0.74 ± 0.27
Grande Prairie	4N	Low[4]	Low	Poor	1.19 ± 0.09	0.35 ± 0.22
	6N	Low	High	Poor	2.17 ± 0.37	0.20 ± 0.18
	C	None	None	Fair	2.14 ± 0.31	0.47 ± 0.27
Brooks	1N	V.High[5]	Low	V.Poor	1.16 ± 0.48	0.03 ± 0.05
	3S	Low[6]	Low	Fair	2.54 ± 0.48	0.16 ± 0.10
	8S	Low	High	Poor	2.20 ± 0.46	0.07 ± 0.08
	C	None	None	Fair	2.86 ± 0.39	0.58 ± 0.21

1 Application = 4.2 + 1.6 + 2.3 m^3 per plot (135 m^2) in 1982, 1984, and 1985, respectively.
2 Application = 6.2 m^3 per plot (135 m^2) in 1982.
3 Application = 12.5 m^3 per plot (135 m^2) in 1982.
4 Application = 2.7 + 6.0 m^3 per plot (135 m^2) in 1982 and 1984, respectively.
5 Application = 5.6 + 2.9 m^3 per plot (135 m^2) in 1983 and 1984, respectively.
6 Application = 2.8 m^3 per plot (135 m^2) in 1983.
7 See Peake et al. (1985) and Peake and Connery (1986).
8 Based on visual field estimates.
9 NA = not applicable as control area not planted.

soils was similar to the field but the reduction in plot 6N as compared to 2N was more extreme in the field (60 versus 30% reduction). Growth in the Grande Prairie soil was good in the greenhouse although it was sparse in all plots in the field. Barley grew well in soil from the Brooks plots 3S, 8S and the control even though growth in the field in plot 8S was poor. In soil from Brooks plot 1N in which the plants in the field were barely visible, growth was moderately good.

Alfalfa exhibited much less growth than barley in all 14 soil-sludge combinations. However, the growth of alfalfa in the greenhouse much more closely reflected the growth patterns seen in field situations. Growth in the greenhouse was best in the control soils taken from all four sites and poorest in the same soils that gave the poorest growth in the field.

3.4 DISCUSSION

It is apparent from this study that land used for the disposal of oily wastes can support good crop growth. However, soil subjected to certain sludge treatments remained highly unproductive due to one or more chemical factors. Two factors which may have been expected to affect productivity recovery time, fertilization and cultivation, did not appear to be major influences. However, zero fertilizer and zero tillage treatments were not included in the experimental design and these factors still may be important in determining decomposition rates.

Total sludge application rates at Lloydminster were generally poor indicators of crop growth but total oil content remaining in the soil proved to be a much more useful predictive parameter. Crop growth was generally good when total oil content was 3.5% or lower and was almost always poor when the oil content exceeded 5% (see Section 4.8.2.8). These relationships are not absolute as they are modified by other soil and plant characteristics. The other prime factor that may have influenced barley growth was salt concentrations in the soil, especially chloride levels. As seen in Figure 12, best growth was obtained when both oil content and chloride concentrations were low. When the oil content was less than 2.8% and chloride content less than 22 meq.L^{-1}, growth was good. When the oil content was between 3 and 4%, high chloride levels apparently restricted growth.

Total salts, as indicated by electrical conductivity, were lowest in plots 1W, 8W and the control, the identical areas in which oil content was lowest and barley growth the greatest. Indeed one of the distinctive chemical characteristics of the 8W plot was the unusually low (for Lloydminster) chloride concentrations. Although unproven, residual oil concentrations and chloride levels appear to be major parameters to be used for predictions of soil productivity. The apparently different response of barley in the greenhouse and the field would appear to contradict the idea that oil residue and salts were major growth controlling factors. However, the general success of barley in the greenhouse could have been due to the use of a different variety there than in the field (Diamond versus Bonanza). Recent work has shown that barley is extremely variable with regard to salt tolerance (D. McCoy, pers. comm.) and may exhibit similar variability with regard to other stress factors. The much closer correlation between field and greenhouse performance when alfalfa was used would support the importance of plant factors when evaluating productivity recovery time.

A second major question that arose from the Lloydminster field data was why the residual oil contents varied so much among plots which had been treated with identical quantities of oil and also why plots treated with different quantities of oily wastes had similar oil contents in 1986. Assuming the application treatments were relatively accurate, the quantities of residues should be dependent on decomposition rates, as little or no oil was detected in the groundwater or surface water (Peake et al. 1985, Peake and Connery 1986). However, the factors responsible for the different rates of decomposition are unclear.

As an example of apparent differential rates of decomposition, the four plots on the western portion of the site which had received the lowest amount of sludge contained 2.6% (1W) 4.0% (4W), 5.5% (6W) and 5.2% (7W) oil residues. The plot with the second lowest residue content was 8W (3.4%) which had a moderately heavy application of sludge. As 1W and 8W were located at the high ends of the experimental

area, there is a possibility that drainage position may have influenced decomposition even though total relief was small. However, the plot containing the highest residual oil levels (8.6%) was 8E which also occupied a good drainage position. The eastern plot with the least oil content was 1E and the plots receiving identical oil treatments contained much more oil (3.6% versus 7.1% - 4E, 5.1% - 6E and 6.8% - 7E).

It is apparent that at Lloydminster the decomposition of oily sludges is not predictable and in turn rehabilitation of the total site for agricultural uses has an unknown time factor. It is clear, however, that crops can be grown on soils which have received relatively large amounts of oily wastes. In that good growth is possible, it is imperative that careful risk assessments be made of the plant material to determine if the land can be returned to agricultural uses.

At Drayton Valley the growth of timothy followed a more predictable pattern than that of barley at Lloydminster, i.e. growth was satisfactory in low sludge treatment plots and poor where high levels of sludge had been applied. The 1986 monitoring suggests that the use of a high rate of fertilizer may have enhanced plant growth, perhaps via increased oil decomposition rates. However, quantitative yield assessments as well as residual oil measurements on all the plots would be required to confirm this finding. In that the surrounding area is being used by Pembina in a full scale landtreatment operation, it may be desirable to determine if fertilizer or oil content benchmarks can be determined at Drayton Valley. The situation is somewhat simplified as salts were present at much lower concentrations compared to Lloydminster.

At Grande Prairie and Brooks, plant growth was unsatisfactory in all the treatments. However, it must be noted that with the hay and dryland pasture species planted, good production does not normally occur until the second growing season. It was apparent from the greenhouse study that the control and low level treatment soils from both areas had the potential to support moderate to good plant growth. Further observations are required to clarify sludge application soil - plant relationships.

4. OIL CONTENT, CHEMICAL ANALYSES AND PLANT UPTAKE

4.1 OBJECTIVES

The effectiveness of biodegradation as a mechanism for oily waste treatment can be evaluated by following the changes in oil content of the soil. The objectives of the present study were to continue monitoring the disappearance of oil at the Lloydminster and Drayton Valley sites, and to investigate the chemical nature of the residual oil.

Since crops were grown on the sludge-treated soils for the first time in 1986, the potential uptake by plants of toxic or carcinogenic compounds, some of which are known to occur in heavy oils, becomes a genuine concern. A further objective, therefore, was to devise and implement a scheme of risk assessment to be used with agricultural crops.

4.2 MATERIALS AND METHODS

4.2.1 Sample collection

4.2.1.1 Soil samples. Both the Lloydminster and Drayton Valley sites are divided into 16 plots, each plot having received varying quantities of sludge and fertilizer. Soils were collected from five sampling points within each plot. At Lloydminster, soils were taken from all 16 plots, resulting in 80 soil samples, while at Drayton Valley soils were obtained from only four plots, resulting in 20 soil samples. Control soils were removed from the border area and were supposed to have been oil-free. Soils were stored in plastic bags at 5°C.

4.2.1.2 Plant samples. Plant uptake studies were carried out only on the Lloydminster site crop. The barley growing within a one square metre area was cut as close as possible to the soil sampling positions. For further details, see Section 3.2.1.2

4.2.2 Sample preparation

4.2.2.1 Soil samples. All soil samples were processed through a 2 mm sieve. Aggregates too large to pass through were transferred to a mortar and crushed. Stones and pieces of plant material were removed by hand. Unsievable material ranged from 3 to 10% of the total soil weight. Sieved samples were packaged in fresh plastic bags and stored at 5°C.

4.2.2.2 Plant samples. Plants were cleaned, cut, dried and finally pulverized. For additional information, see Section 3.2.1.2.

4.2.3 Sample extraction

4.2.3.1 Extraction for oil content measurement. Each of the 80 soil samples from the Lloydminster site and the 20 from the Drayton Valley site were extracted with toluene using a conventional Soxhlet apparatus incorporating a Dean-Stark trap to separately collect water. The soil sample size varied from 25 to 30 g. This procedure produces a soil which is free of water and sources of organic carbon, and is necessary for the subsequent determination of the oil content.

4.2.3.2 Extraction for chemical analysis. Three samples from Lloydminster were singled out for more extensive examination. Soils from plots 1W and 4W, which were selected for the greenhouse study, were also chosen for chemical analysis in an attempt to correlate the observed growth to the chemical content. These two soils, plus a control, were extracted with toluene in the usual Soxhlet (Dean-Stark adapted) apparatus; a sample size of 125 g, containing 25 g from each of the five replicates within the plot, was used.

4.2.3.3 Extraction for plant uptake analysis. Plants grown on Lloydminster plots 1W and 4W were analyzed for the uptake of organic compounds. Barley from the border control area was not included since

that soil was found to be contaminated with oil. Two representative plant samples were prepared by combining equal weights (5 g) of dried plant material from each of the five sampling points within the plot. These 25 g plant samples were then homogenized using a Brinkman Polytron, following an EPA procedure developed by Coates et al. (1985). Each sample was homogenized in three portions (2 x 8 g, 1 x 9 g) in a 200 mL high-walled beaker with 75 mL of acetonitrile. The Polytron generator was then immersed in the solvent until it was slightly less than 1 cm from the bottom. The rheostat was brought gradually up to 80% of the maximum setting and was maintained for 2 min. On termination, the generator was removed and rinsed with acetonitrile before proceeding to the next portion. Fresh acetronile was added for each homogenization step.

4.2.4 Sample fractionation

4.2.4.1 Fractionation for chemical analysis. The oil from the three soil samples was recovered in toluene after approximately 3 h of Soxhlet extraction. The toluene was removed by rotary evaporation, and a constant weight established. Residual soil was dried and weighed. Soil moisture volumes, as measured in the Dean-Stark trap, were recorded.

The oil was redissolved in a small amount of toluene (1 g oil: 1 mL toluene) and a ten-fold excess of hexane was added to precipitate the asphaltenes. The asphaltenes were removed by filtration. The solvent was evaporated from the remaining maltene fraction which was then chromatographed on silica gel to separate the oils from the resins. First hexane, followed by methylene chloride and finally freshly distilled THF (tetrahydrofuran) were used to elute the oils, a less polar and a more polar resin fraction, respectively. The weights of silica gel used were in excess of ten times the maltene weight. All soluents were removed by rotary evaporation, and constant weights established.

The oils were further fractionated into aliphatics and aromatics by chromatography on 25 g alumina (previously baked at 300°C for 1 day) with pentane as the eluent for the aliphatics and benzene for the aromatics. Solvents were removed by rotary evaporation.

4.2.4.2 Fractionation for plant uptake analysis. The homogenized samples were transferred into 50 mL centrifuge tubes (filled to approximately 40 mL) and centrifuged for 10 min. The centrifugate was decanted. Fresh acetonitrile was added to the remaining plant solids, the entire contents of the tube stirred and then recentrifuged. The supernatant liquid was decanted and added to the first extract.

The extraction procedure as described by Coates et al. (1985) was scaled up 2½ times. Pentane (125 mL) was added to the separatory funnel containing the acetonitrile extract (ca. 250 mL), and shaken for approximately 1 min. Water saturated with sodium chloride (25 mL) was then added, followed by 875 mL of double-distilled water. After shaking again for about 1 min, the phases were allowed to separate. The pentane layer was collected and run through a glass filtering funnel containing anhydrous Na_2SO_4 (previously baked at 500°C for several hours and cooled) to a depth of 2.5 cm. The pentane was then taken off by rotary evaporation until ca. 2 mL remained.

Although Coates et al. (1985) recommended passing the pentane extract through a microcolumn of silicic acid, it was found that the elution rate in such columns was so slow that the chromatographic separation would probably have required several days to complete. Instead, it was decided to resort to chromatography on alumina (10 g, neutral activity). Three fractions were collected; the first was eluted with pentane (30 mL), the second and third with an 85%:15% mixture of pentane and methylene chloride (2 x 30 mL). This procedure should remove the aliphatic, aromatic and polar components, in that order.

4.2.5 Sample analysis

4.2.5.1 Oil content analysis. Carbon contents of the soils were measured using a LECO CR 12 Carbon Determinator. Both oil-containing and oil-free (extracted with toluene) soils were analyzed. The difference in carbon content can be related to the oil content, and an oil: solids ratio can be calculated.

4.2.5.2 Chemical Analysis. The aromatic fractions obtained from the oil extracted from the soils of Lloydminster plots 1W , 4W and the control area were analyzed by gas chromatography with flame ionization detection (GC/FID). GC conditions were as follows:

injector temperature	250°C
detector temperature	250°C
initial temperature	50°C
hold time	2 min
program rate	5°C/min
final temperature	250°C
hold time	10 min
run time	52 min

The gas chromatograph (Varian 3400) contained a 15 m SE 54 narrow bore capillary column. Sample volumes were adjusted depending on organic content; volumes trended to be in the range of 3 to 4 mL. Pentane was used as the solvent. Injections were 0.5 µl.

4.2.5.3 Plant uptake analysis. A total of six fractions (three each from plots 1W and 4W) were investigated by GC/FID. The instrument and conditions were identical to those described in the preceding section. Sample volumes varied between 100 to 250 µl. Injections were 0.5µl.

Since the major concern was to assay the possibility of uptake of polynuclear aromatic hydrocarbons, only the two supposedly aromatic fractions (one each from plot 1W and 4W) were considered worthy of GC/MS characterization. Analyses were carried out on a Finnigan 4500

GC/EI Mass Spectrometer System. The gas chromatograph was fitted with a 30 m SE 54 wide bore capillary column. The GC conditions differed slightly:

injector temperature	275°C
initial temperature	50°C
hold time	1 min
program rate to 100°C	20°C/min
program rate above 100°C	5°C/min
final temperature	300°C
hold time	10 min
run time	53.5 min

Sample volumes were 120 µl for the 1W aromatic fraction and 250 µl for the 4W aromatic fraction. Injections were 0.5 µl.

4.2.6 Asphaltene precipitation

Asphaltene contents were measured for all 16 plots of the Lloydminster site. This quantity had already been determined for the residual oil in plots 1W, 4W and the control area (see section 4.2.4.1) so the remaining 14 plots were then examined. The Soxhlet extractions were carried out on a smaller scale, using only 30 g of soil (6 g from each of the 5 subsamples). The asphaltene contents obtained in this manner represent an average of the five replicates. The usual procedure was followed: extraction with toluene, rotary evaporation of the solvent, and establishment of a constant weight. The oil was redissolved in toluene (1 g oil: 1 mL toluene), and a ten-fold excess of hexane was added. The asphaltenes were collected in a glass filtering funnel under vacuum. Once dried, a weight was obtained and the corresponding percentage of asphaltenes in the oil calculated.

4.3 RESULTS

4.3.1 Residual oil contents of the soil

4.3.1.1 Lloydminster. Oil to solid ratios were determined for 80 soil samples collected from all 16 Lloydminster plots. The results for the five replicates from each plot were averaged, yielding one characteristic oil content value for each subplot. These data are combined with details of the magnitude of the sludge and fertilizer treatment, and with a visual assessment of the growth, and presented in Figure 10. Sludge applications were ranked as low (L), medium (M) or high (H), while fertilizer applications were classified as either high (H) or low (L). Good growth occurred only (but not always) in plots in which average oil contents were less than 3.6%. Once oil contents exceeded 5%, growth was poor.

4.3.1.2 Drayton Valley. Oil to solid ratios were evaluated for 20 soil samples taken from four Drayton Valley subplots (2N, 3N, 4N and 6N). Oil contents of the five samples for each of the plots were averaged, and are presented in Figure 11 along with the sludge and fertilizer applications, and the growth appraisal. In general, growth was inversely related to oil content with good growth in plots with less than 2.8% oil.

4.3.2 Productivity versus oil content

4.3.2.1 Lloydminster. The weights of dried barley can be matched to the oil content of the soil in which it was grown. Plant material was collected at five sampling points within four plots. Rather than averaging the data derived from each plot, the information from each sampling point is shown in Table 19. A plot of plant weight against oil content (Figure 12) reveals a trend of decreasing productivity with increasing oil content that is not only self-evident, but quite dramatic. Oil contents of more than 4% in the soil resulted in extremely poor growth with one exception; that being from an area in

	Sludge Application	Fertilizer Application
	% Oil Content	Growth
	East	West
Plot 1	M L 3.59 Good	L L 2.61 Good
Plot 2	H H 5.95 Fair	M H 5.26 Poor
Plot 3	H L 5.97 Poor	M L 4.85 Poor
Plot 4	M H 7.05 Poor	L H 4.01 Fair
Plot 5	H L 7.88 Poor	M L 5.22 Poor
Plot 6	M H 5.12 Fair	L H 5.46 Poor
Plot 7	M L 6.83 Poor	L L 5.16 Poor
Plot 8	H H 8.58 Poor	M H 3.38 Good

Figure 10. An overall view of the sludge and fertilizer application, oil contents and growth assessment at the Lloydminister site.

Sludge Application	Fertilizer Application
% Oil Content	Growth

	North		South	
Plot 2	L 2.00	L Good	M N.M.	L Good
Plot 3	L 2.76	H Good	M N.M.	H Good
Plot 4	M 2.98	H Fair	H N.M.	H Poor
Plot 6	M 3.83	L Poor	H N.M.	L Very Poor

N.M. = not measured

Figure 11. An overall view of the sludge and fertilizer application, oil contents and growth assessment at the Drayton Valley site.

Table 19. Relation between air-dry weights of barley and the soil's corresponding oil content at the Lloydminster site.

Sample	Seed Weight (g)	Whole Plant Weight (g)	% Oil Content
Plot 1W -1	121.4	246.2	2.44
-2	87.1	165.4	2.82
-3	66.8	139.6	2.92
-4	120.5	259.3	1.86
-5	44.0	93.1	3.01
Plot 4W -1	21.1	45.1	3.44
-2	12.8	28.7	3.60
-3	39.6	84.9	3.94
-4	13.3	29.7	3.03
-5	1.9	10.4	6.03
Plot 5W -1	0	11.9	3.56
-2	0	4.2	5.95
-3	0	0.5	5.77
-4	0	4.5	4.06
-5	0	2.3	6.77
Plot 8W -1	92.8	173.5	3.80
-2	258.8	536.7	3.28
-3	331.1	727.3	2.28
-4	56.0	103.9	4.84
-5	182.1	378.6	2.72

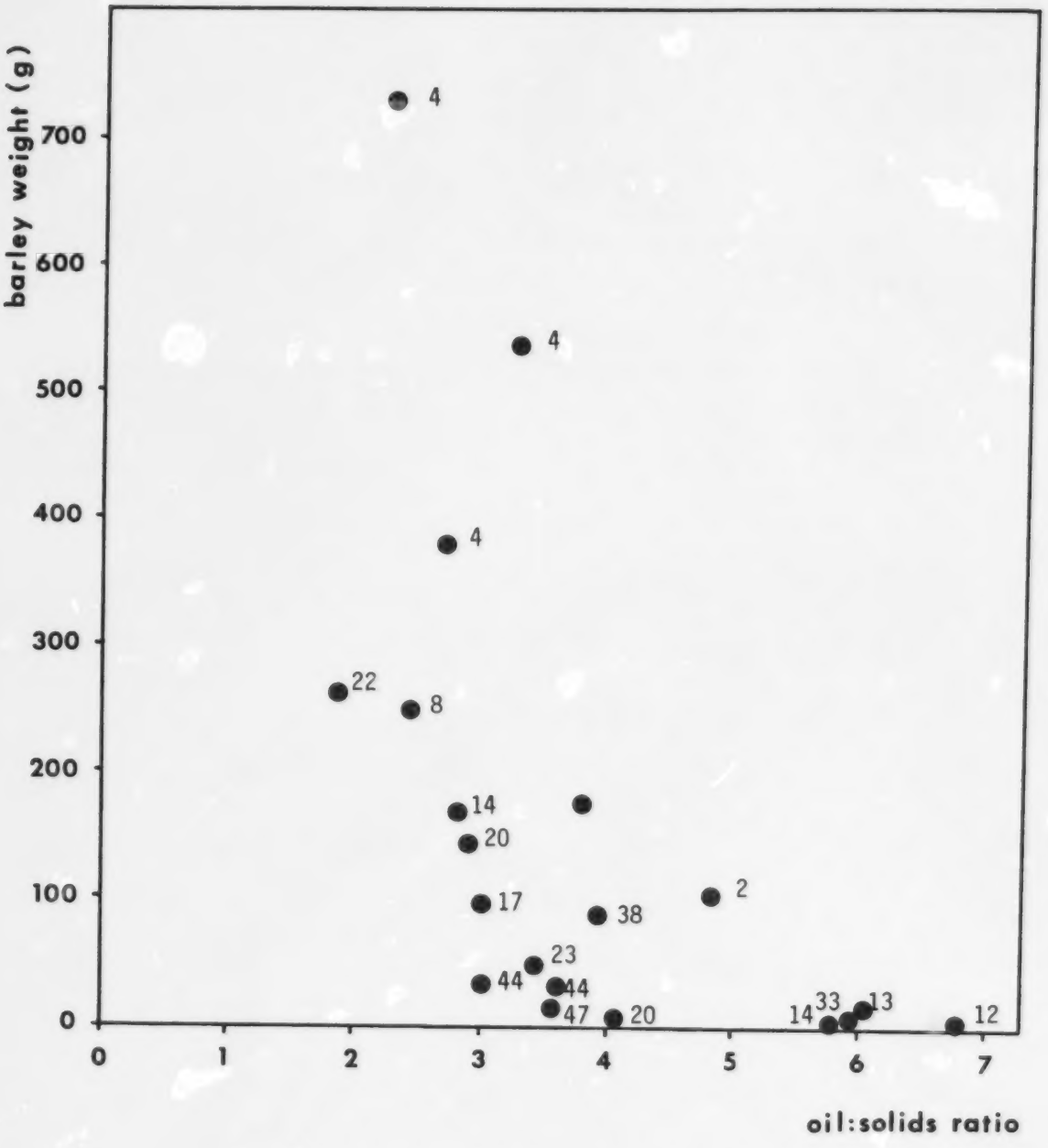


Figure 12. Dependency of plant productivity on the corresponding oil content of the soil at the Lloydminster site. Numbers are chloride concentration (meq.L^{-1}) of saturated water extracts.

plot 8W which was not seeded properly. Chloride concentrations are also represented in Figure 12 and discussed in Section 3.4.

The productivity of the control regions could not be related to their respective oil contents since these were not determined on an individual basis. Only an average oil content representing five sampling points was measured; surprisingly, the control soils contained 1.26% oil. Not having a contamination-free control soil is unfortunate from the point of view of making comparisons, especially with regards to the greenhouse and the plant uptake study. The emphasis of the plant uptake study had to be altered for this reason.

4.3.2.2 Drayton Valley. The yield of dried hay can be paired with the corresponding oil content of the soil. Four subplots were sampled, at five positions within each. The unaveraged data appear in Table 20 and are plotted in Figure 13. There is an obvious drop in productivity at a soil oil content of approximately 4%. Once oil contents were below 2.5%, growth of hay was good (note that two samples with low oil content were taken from areas that were not planted properly). Hay was not harvested on plots having received a wide variety of treatments, so the quantitative relationship between productivity and oil content remains to be refined.

4.3.2.3 Generalized relationship between oil content and plant growth. If the plots are grouped according to their observed growth (as opposed to measured growth) and the oil contents of those plots exhibiting roughly the same growth are averaged, then a simplified diagram showing an approximate relationship between growth and oil content can be created. Figures 14 and 15 show this correlation for growth at the Lloydminster and Drayton Valley sites, respectively. It is suggested from the Lloydminster data that growth may be good if the oil content of the soil is less than ca. 3.5%, fair in the range of 3.5 to 5%, and very poor above 5%. Based on the Drayton Valley information, these values are all shifted down: good growth below 2.5%, fair growth from 3 to 4%, and poor growth above 4%. These benchmark numbers will change with differences in salt concentrations (see Section 3.4).

Table 20. Relation between dry weights of hay ($g \cdot m^{-2}$) and the soil's corresponding oil content at the Drayton Valley site.

Sample	Whole Plant Weight (g)	% Oil Content
Plot 2N -1	44.5	1.79
-2	199.5	2.06
-3	189.5	2.02
-4	186.1	2.12
-5	160.5	2.02
Plot 3N -1	53.8	1.48
-2	225.8	2.97
-3	96.4	3.70
-4	117.5	3.10
-5	229.5	2.53
Plot 4N -1	66.9	3.14
-2	365.8	2.54
-3	68.8	3.10
-4	148.2	3.17
-5	124.0	2.94
Plot 6N -1	106.2	2.86
-2	74.9	3.84
-3	17.6	4.44
-4	65.9	4.02
-5	28.8	4.01

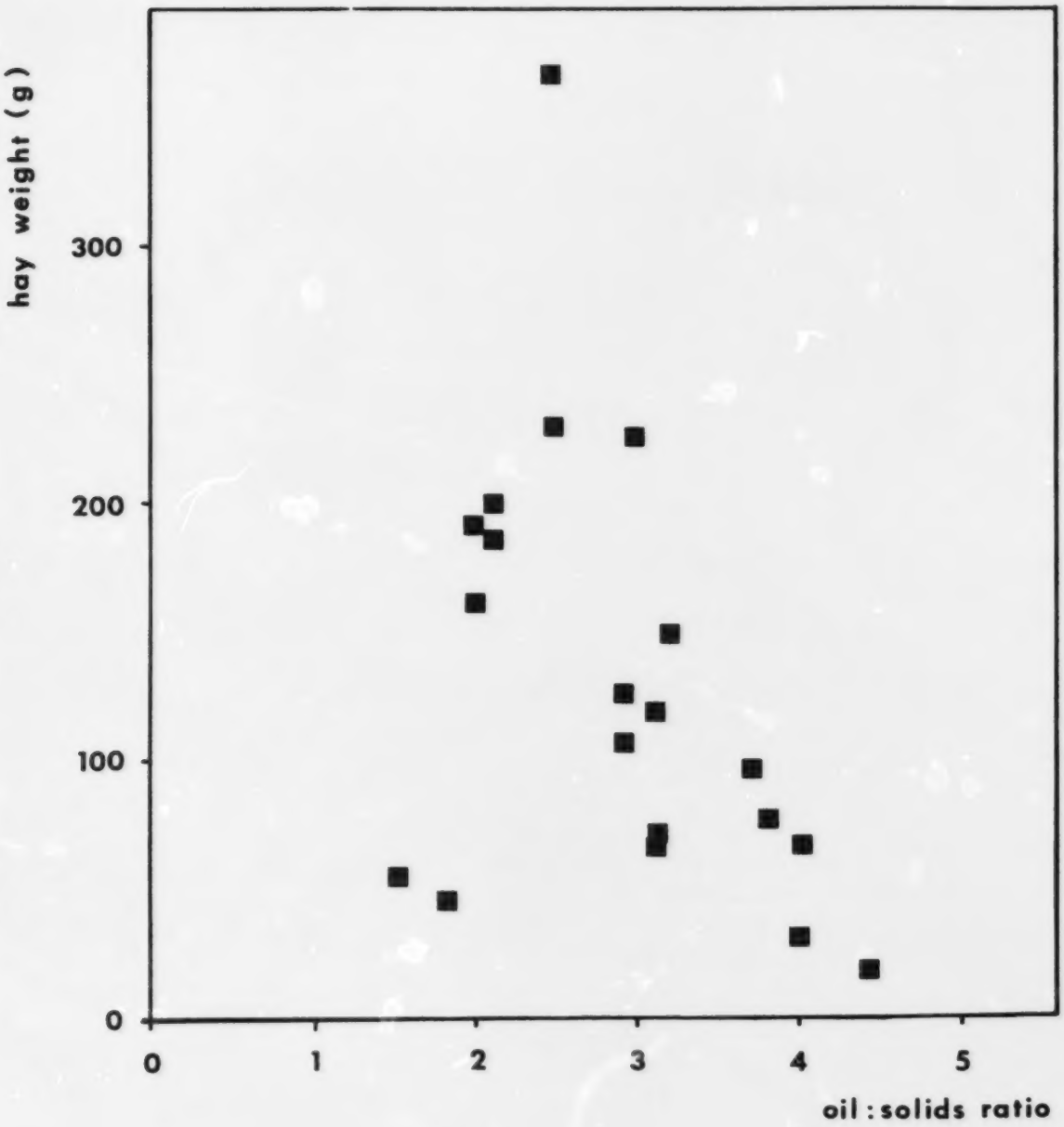


Figure 13. Dependency of plant productivity on the corresponding oil content of the soil at the Drayton Valley site. The two data points at the lower left was obtained from samples that were not seeded properly.

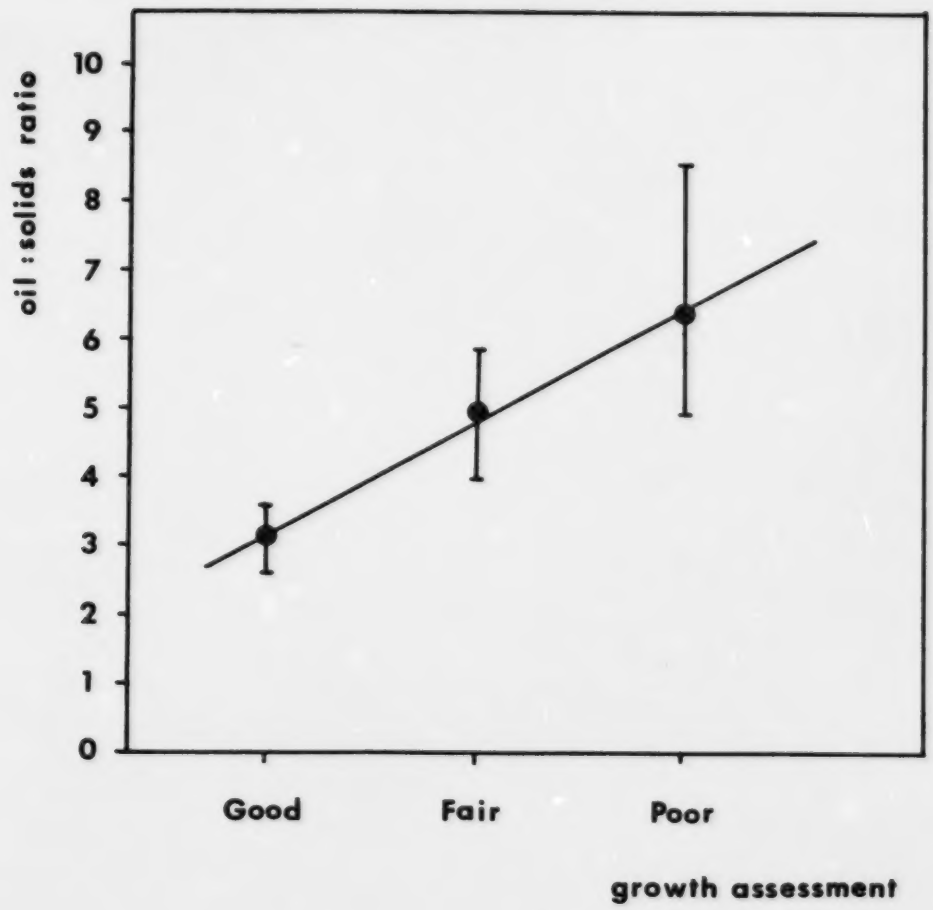


Figure 14. Approximate correlation between observed growth of barley and soil oil content based on Lloydminster data.

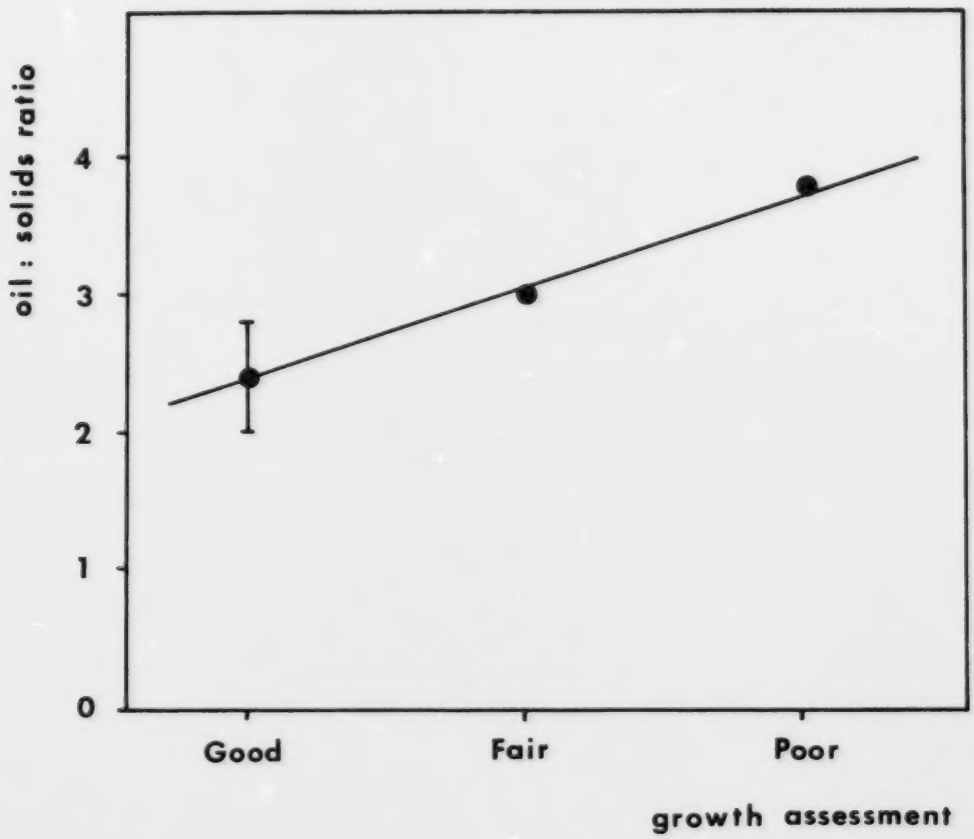


Figure 15. Approximate correlation between observed growth of hay and soil oil content based on Drayton Valley data.

4.3.3 Degradation of the oil

4.3.3.1 Lloydminster. Oil contents, as determined in September 1986, are compared with the last measurements made in October 1985 (Table 21). A positive value in the percent degradation column indicates an apparent gain of oil in the last year, while a negative value signifies an apparent decrease in oil. Since no oil has been added since the spring of 1985, any apparent increases are due to either underestimates in 1985 or overestimates in 1986. The estimates made in 1986 appear to be good as variation in oil contents within the plots is relatively small.

Differences in sample preparation prior to 1986 and in 1986 would result in apparent increases in oil content. Prior to 1986, samples were not sieved and the gravel-sized material was left in the samples. In 1986, 4 to 10% of the soil exceeded 2 mm and was discarded. In addition, in 1986 all lumps of oily sludge were crushed and included in the analysis. Prior to this, large lumps of sludge were apparently discarded. Both of these factors contributed at least partially to the apparent increases in oil content. In all 16 treatments there was approximately a 4.6% increase; this would be more than counterbalanced by discarding gravel-sized material. Thus, it would appear that biodegradation is occurring but the rate is unknown.

4.3.3.2 Drayton Valley. Less information is on hand from the Drayton Valley site than the Lloydminster site since fewer plots were sampled. Oil contents were last measured in October 1984, and these data are compared with those of October 1986 (Table 22). As with the Lloydminster site, the apparent "increases" in oil supersede the decreases. The factors accounting for this are the same as with the Lloydminster soils. No conclusions can be drawn with regard to rates of oil biodegradation.

4.3.4 Chemical Analyses of the Oil

Oil was extracted from Lloydminster plots 1W and 4W, plus a control region, and was fractionated into five classes: asphaltenes, resins (2), resins (1), aliphatics, and aromatics. Resin (2) differs

Table 21. Degradation of oil at the Lloydminster site since October 1985.

Plot	Oil:Solid Ratio[1] (Oct. 15, 1985)	Oil:Solid Ratio (Sept. 4, 1986) ($\bar{x} \pm SD$)	% Degradation
1W	2.42	2.61 ± 0.47	+ 7.6
2W	5.10	5.26 ± 1.04	+ 3.3
3W	4.97	4.85 ± 0.71	- 2.4
4W	3.03	4.01 ± 1.18	+32.1
5W	7.27	5.22 ± 1.36	-28.2
6W	4.50	5.46 ± 1.47	+21.5
7W	4.41	5.16 ± 0.71	+17.1
8W	2.81	3.38 ± 0.99	+20.6
1E	3.97	3.59 ± 0.61	- 9.6
2E	6.78	5.95 ± 0.51	-12.2
3E	6.80	5.97 ± 0.61	-12.3
4E	6.73	7.05 ± 0.87	+ 4.7
5E	7.21	7.88 ± 1.07	+ 9.3
6E	4.78	5.12 ± 0.99	+ 6.9
7E	6.96	6.83 ± 0.83	- 1.9
8E	7.34	8.58 ± 1.30	+16.9

[1] Data from Peake and Connery (1986).

Table 22. Degradation of oil at the Drayton Valley site since October 1984.

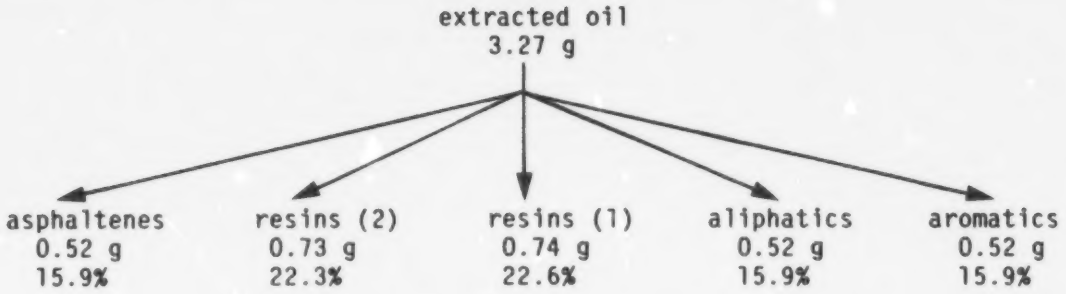
Plot	Oil:Solid Ratio[1] (Oct. 1984)	Oil:Solid Ratio (Oct. 1986) $\bar{x} \pm SD$	% Degradation
2N	1.69	2.00 ± 0.21	+18.3
3N	2.20	2.76 ± 0.83	+25.5
4N	3.07	2.98 ± 0.26	- 2.9
6N	4.68	3.83 ± 0.59	-18.2

[1] Data from Peake et al. (1985).

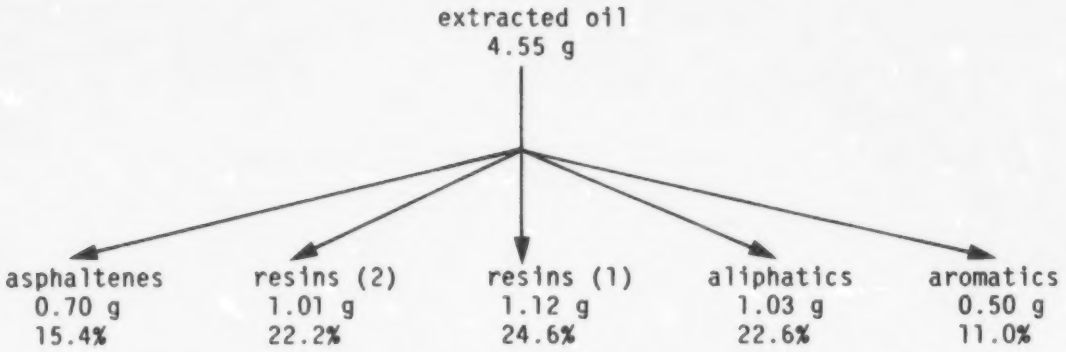
from resin (1) in that it is more polar than resin (1). The distribution of these components in the three oil samples is shown in Figure 16. Some small losses were incurred, but this is to be expected in such involved separation schemes.

The asphaltenes and two resin fractions cannot be easily studied for chemical content since their average molecular weights are generally too high and their structures too complicated to be interpreted by GC/MS. Investigation of the aliphatic fraction is usually not very informative so was not pursued; on the other hand, the aromatic fraction is normally the one of most interest and concern since most deleterious organic substances tend to fall into that category. Analysis by GC/FID of the three aromatic fractions revealed only huge, unresolved envelopes of peaks. Further analysis of such complex systems by GC/MS would be futile without some additional simplification. GC/MS might provide some very basic information such as some structural features, but would not likely reveal definitive structures. A possible explanation for the observed complexity of the aromatic fraction is that not enough alumina was used in the chromatographic separation, resulting in some aliphatics eluting along with the

PLOT 1W



PLOT 4W



CONTROL PLOT

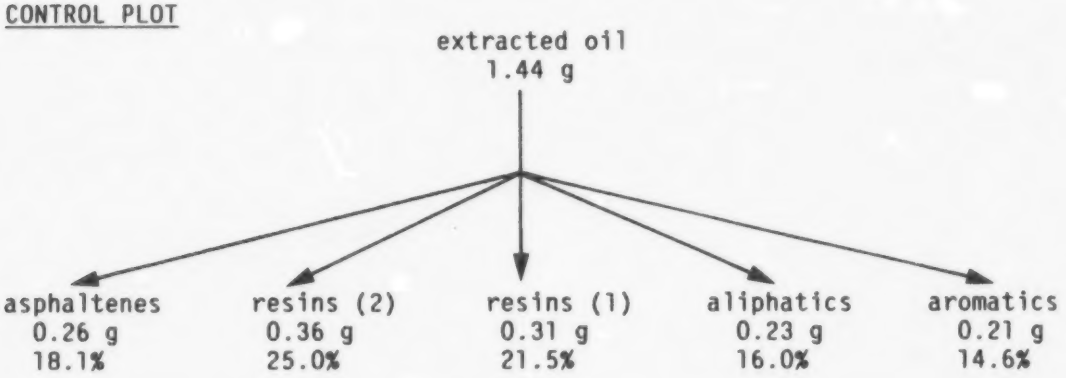


Figure 16. Distributions of asphaltenes, resins, aliphatics, and aromatics in three Lloydminster residual oils.

aromatics. If this is the case, then rechromatography would be the simplest solution in future analyses. Perhaps using hexane instead of pentane as the eluent would more efficiently remove the aliphatics. On the contrary, if the aromatic fraction does not contain aliphatics, then a structural analysis may prove to be extremely difficult, if not impossible.

4.3.5 Plant Uptake

Since it was discovered that the control soil at Lloydminster was contaminated with oil, the original plan of comparing plants grown on sludge-treated soil to those grown on oil-free soil had to be abandoned. Instead, it was decided to examine plants grown on soils which correspond to regions of good and poor growth. Plots 1W and 4W were selected since they meet the above requirements. Although this plan of action cannot confirm the possible natural existence of polynuclear aromatic hydrocarbons (PAH's) in the barley grown at the Lloydminster site, it should shed some light on whether uptake (if any) can be linked to the respective oil contents of the soils, as well as allow the EPA procedure to be tested.

Three fractions were obtained from each of the plant extractions, tentatively labelled as aliphatic, aromatic, and polar. All six samples underwent GC/FID analysis. Plot 1 aliphatics revealed a huge, unresolved envelope of peaks typical of aliphatic hydrocarbons. Plot 4 aliphatics contained few components and did not show the typical "hump" pattern as seen for Plot 1. Plot 1 and Plot 4 aromatics showed a preponderance of peaks, and both of these were further studied by GC/MS. Plot 1 and Plot 4 polars both had a repetition of peaks seen in their respective aromatic fractions, indicating that the elution procedure was not effective.

Results from the GC/MS analysis were rather disappointing. There was no evidence of any PAH's; a computer-assisted ion search for a whole series of PAH's and alkylated PAH's was undertaken and still no hint of their existence could be found. The following types of compounds were identified: alkanes, alkenes, aliphatic methylketones, and

alkyl-substituted cyclo-alkanes and -alkenes. Also found was a series of aliphatic nitriles, but these undoubtedly stem from the acetonitrite solvent. In future, the solvent should be purified before use, and a blank run conducted to trace the source of impurities. Only the Plot 4 aromatic fraction exhibited evidence of terpenoid structures, and either diphenylamine or N-nitrosodiphenylamine (both mass spectral fragmentation patterns are very similar,, plus two isomeric forms of ethylphenol. The two ethylphenols and the N-nitrosodiphenylamine are present in the dried plant matter at levels of approximately 0.05, 0.05 and 0.02 ppm, respectively.

4.3.6 Asphaltene Content

Asphaltene contents were determined for each of the 16 Lloydminster subplots. These values are listed in Table 23, not only as a percentage of the extracted oil, but also as a percentage of the soil itself.

The consideration of the asphaltene content of the soil is important since the proportion of asphaltenes in the oil alone does not necessarily imply a similar proportion in the soil. For instance, Plot 5E shows only 17.4% asphaltenes in the residual oil (which is one of the lowest values), yet the oil content is one of the highest, so the actual quantity of asphaltenes existing in the soil is very high (1.4%).

4.4 DISCUSSION

4.4.1 Oil and asphaltene contents

Landtreatment as a means of disposal of oily wastes depends upon the efficiency of biodegradation by soil microorganisms. This degradation, in turn, is affected by a wide variety of factors, including the type of soil, the climatic conditions, nutrient sources, the nature and amount of the oil as well as inorganic salts, and extent of cultivation. Continued monitoring of the oil content is fundamental in deciding upon the future of these landtreatment sites. The evidence

Table 23. Asphaltene contents of each subplot of the Lloydminster site.

Plot	% Asphaltenes in Oil	% Asphaltenes in Soil
1W	15.30	0.41
1E	21.54	0.77
2W	19.31	1.02
2E	19.58	1.17
3W	19.29	0.94
3E	18.27	1.09
4W	15.38	0.62
4E	17.64	1.24
5W	18.46	0.96
5E	17.42	1.37
6W	18.45	1.01
6E	21.88	1.12
7W	20.62	1.06
7E	20.34	1.39
8W	18.53	0.63
8E	19.81	1.70

derived from the Lloydminster and Drayton Valley sites points towards an apparent reduction in rates of biodegradation. Such an observation is too premature as different methods of sample preparation have resulted in data which is difficult to compare. Nevertheless, it is a survey which ought to be continued.

A more tangible statistic to emerge from the oil content measurements was the apparent link between plant growth and soil oil content. Limits on the amount of growth to be expected for soil containing a given proportion of oil could be established. These limits differed between the Lloydminster and Drayton Valley sites; for instance, poor growth was generally seen at Lloydminster when the soil oil content exceeded 5%, while at Drayton Valley poor growth was observed when the residual oil content was above 4%. Such variations are to be anticipated where disparate types of soils, oily sludges and crops are involved.

Asphaltenes should be the least degradable component of the oil. As the more easily degradable oil is depleted by the soil micro-organisms, a gradual accumulation of asphaltenes is foreseen; however, this scenario has not yet materialized. Asphaltene contents were measured from five Lloydminster soil samples in the autumn of 1985 (Peake and Connery 1986); their average value of 18.7% does not deviate much from the current average (over all 16 subplots) of 18.9%. This similarity may only reflect an insufficiency of data points used for the 1985 average, or may imply that little, if any, biodegradation has taken place.

There was no obvious trend of increasing asphaltene content with increasing magnitude of sludge application, although there did seem to be a correlation between observed growth and asphaltene content. The proportion of asphaltenes in the soil, rather than in the extracted oil, was calculated and matched with the three growth classifications (good, fair and poor) for all 16 subplots. Good growth plots had an average asphaltene content in the soil of 0.60%, fair growth plots of 0.97%, and poor growth plots of 1.18%.

4.4.2 Chemical analysis

Lloydminster plots 1W and 4W were fractionated into asphaltenes, resins, aliphatics and aromatics. A comparison between the respective proportions of these components did not furnish any conclusive evidence. Asphaltene and resin contents were very similar. The aliphatic and aromatic contents showed differences, though, the ratio of aliphatics to aromatics in plots 1W and 4W being 1:1 and 2:1, respectively. Whether this factor is significant, and can in some way be related to the plant growth is not known.

Structural analysis of the residual oil was not successful, and the value of expending much time in pursuing this information is questionable.

4.4.3 Plant uptake

The results from the uptake study suggest that aromatic hydrocarbons are not absorbed by plants, at least at detectable levels. This conclusion must be regarded as tentative since much work remains to be done in this area. The EPA procedure was not followed precisely, but was modified slightly. Coates et al. (1985) recommend the homogenization of fresh plant samples (kept frozen until needed), while the plant matter used in this study was air-dried. Although this would contribute to the potential loss of volatile substances, polynuclear aromatic hydrocarbons, with their very low vapour pressures, should still remain. The use of silicic acid in the chromatography step was altered since the silicic acid packed too closely to allow solvent elution. Use of alumina as a packing material for chromatography to separate aliphatics and aromatics is a standard method to achieve this aim; however, the eluting solvents should probably have been hexane and benzene rather than pentane and a pentane:methylene chloride mixture. Perhaps the latter solvent combinations were adequate for separation on silicic acid, but were decidedly not on alumina.

A few other problems were encountered during the course of this experiment. It was discovered that the acetonitrile solvent used in the homogenization step must first be purified to eliminate contami-

nation by long chain aliphatic nitriles. Evidence for these impurities and others (including plasticizers) materialized during the GC/MS characterization; their absence would simplify the structural analysis process. In future, a blank run must be conducted to ease the recognition of contaminating substances. The lack of plant material grown on oil-free soil also added to the difficulty in interpreting results. Without any control sample for the sake of comparison, the identities of naturally-occurring organics cannot be confirmed. This lack must be remedied.

Coates et al. (1985) reported a successful recovery of 16 different PAH's from spiking experiments using their procedure. It may be advantageous to test our somewhat modified procedure for recovery in the same manner. A non-observance of PAH's in the plant extracts may simply be a reflection of some inadequacy in the procedure. The suitability of the method must be resolved.

The discovery of a couple of phenols in the plot 4 extracts is not surprising since phenols are not only expected by-products of biodegradation but also common constituents of oily wastes. The reason for their appearance in plot 4 and not in plot 1 is not known, but may be related to the presence of standing water in the central portion of the site where plot 4 is located. Since phenols are generally very water-soluble, they may have concentrated in that region. The source of the diphenylamine or N-nitrosodiphenylamine is a mystery, however. The former has uses as an antioxidant and in pesticide production, while the latter is used in the vulcanization of rubber. Spraying of the surrounding crops with pesticides may have been responsible for some diphenylamine drifting onto the site. Why one or the other of these substances should be uncovered only on the one plot can also not be explained. Neither amine is particularly water-soluble, so the presence of either one cannot be connected with the water in the middle of the plot. Further study is required.

5. GROUNDWATER AND SURFACE WATER STUDIES

5.1 OBJECTIVES

The objectives of the groundwater studies were to establish wells and piezometers to determine flow patterns and groundwater depths under the sludge treated plots. Water sampling at different depths will permit monitoring of possible groundwater contamination with either organic or inorganic materials over a long period of time. Surface waters will also be sampled to determine if sludge or fertilizer is affecting runoff water quality.

This section of the report contains preliminary results of the study being conducted by the Earth Sciences Division to establish the effects of landtreatment on groundwater and surface water quality, and to compare these results with results obtained in 1982 through 1985.

5.2 METHODS AND MATERIALS

The study area is located near the city of Lloydminster (Figure 17).

A total of eighteen boreholes at eleven sites were drilled, using a solid stem auger system, to define the shallow geology beneath the plots (Appendix Table 2). Drill cuttings were collected and described at 0.5 m intervals. At one location, a continuous core was collected to facilitate detailed description of geology and structure. Test hole locations are shown in Figure 18 and borehole logs and core description are in Appendix Tables 3, 4, and 5.

5.3 RESULTS AND DISCUSSION

5.3.1 Geology

The site is underlain by fine textured till to a depth of at least 9 m. The till, grey, grading to grey-brown with depth, is dense, plastic and contains numerous pebbles and fine-grained sand lenses. Visual examination of the core from 493 suggests the presence of fractures to a depth of at least 2.5 m. The fracture faces were commonly coated with calcite and/or iron staining.

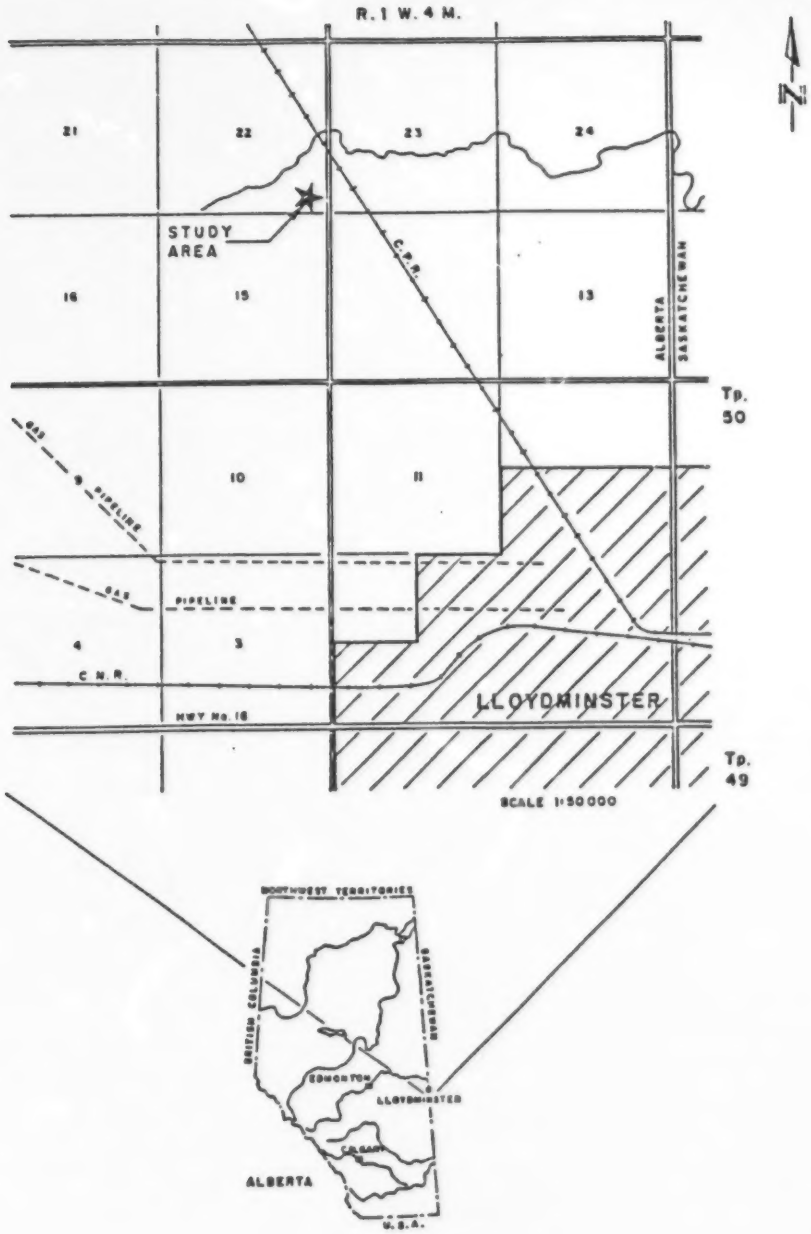


Figure 17. Site of Lloydminster oily sludge treatment plots. Site indicated by star.

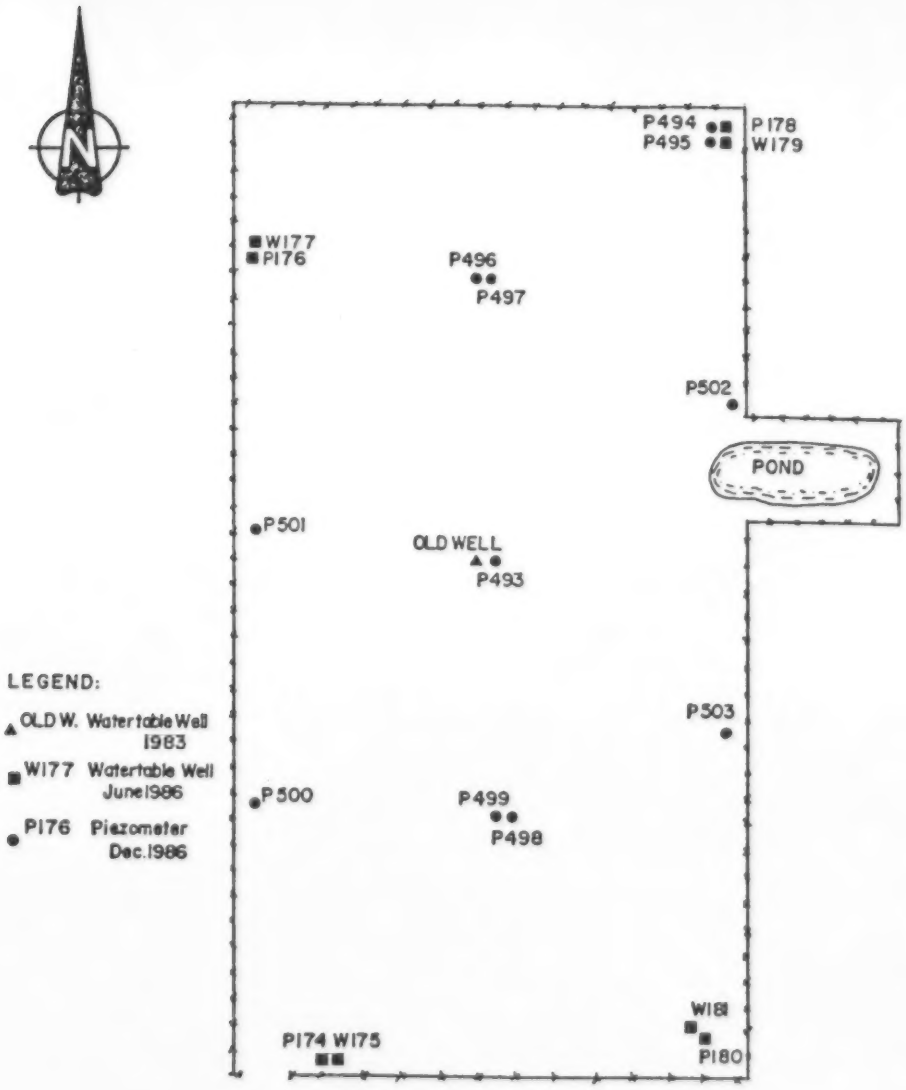


Figure 18. Plan of Lloydminster oily sludge treatment plots and locations of wells and piezometers.

5.3.2 Groundwater flow

Water levels were recorded on eight occasions in monitors installed in June, 1986 and two times in all piezometers. Water level data, presented in Table 24, suggest that the predominant direction of shallow groundwater flow is toward the east under the influence of a shallow hydraulic gradient. A water table contour map could not be constructed since water levels in many of the monitors had not yet reached equilibrium at the last measurement date.

Water level data from the piezometer nest located in the northeast corner of the site indicate that the site in located in a groundwater recharge area. That is, the predominant direction of groundwater flow is downward. A vertical hydraulic gradient of 0.6 is estimated from available data.

Water levels in the water table wells recovered slowly after well installation. During recovery, a noticeable increase in water levels was evident in late July - early August, 1986 (Figure 19). July had unusually high precipitation, indicating that the water table responded relatively quickly to recharge events. Water levels tended to decrease in fall and winter due to a lack of recharge. The annual water table fluctuation was in the order of 1.5 m.

No hydraulic conductivity tests have yet been conducted on the piezometers. Consequently, accurate in-situ hydraulic conductivity (k) data for various geologic materials beneath the site are not available. However, qualitative estimates of k are possible from a visual analysis of the core and from the length of time required for the water level in each monitor to reach equilibrium. Clayey textured till which is fractured or contains lenses of fine grained sand has the highest k value, in the range of 10^{-5} to 10^{-7} cm/sec. The lowest k values, approximately 10^{-8}, are characteristic of till generally deeper than 6 m from surface. Single well response tests are planned for 1987 to obtain quantitative information about in-situ k values. The data will be used to calculate shallow groundwater flow velocities.

Table 24. Water level data.

Well Number	86/06/09 Depth (m)	86/06/09 Elevation (m)	86/07/03 Depth (m)	86/07/03 Elevation (m)	86/07/22 Depth (m)	86/07/22 Elevation (m)	86/08/12 Depth (m)	86/08/12 Elevation (m)	86/09/09 Depth (m)	86/09/09 Elevation (m)	86/12/03 Depth (m)	86/12/03 Elevation (m)	87/01/06 Depth (m)	87/01/06 Elevation (m)	87/02/10 Depth (m)	87/02/10 Elevation (m)
Old well	2.6	98.33	2.0	98.93	1.38	99.55	1.44	99.49	2.8	98.13	2.94	97.99*	3.52	97.41	-	-
W 174	dry	-	8.4	92.72	7.12	94.00	7.44	93.68	6.01	95.11	4.76	96.36*	4.84	96.28	6.08	95.04
W 175	dry	-	5.23	95.92	3.71	97.44	3.66	97.49	2.63	98.52	2.5	98.65*	2.67	98.48	3.45	97.70
P 176	dry	-	9.03	92.20	8.1	93.13	7.48	93.75	5.88	95.35	4.82	96.41*	4.68	96.55	6.17	95.06
W 177	dry	-	5.49	95.84	4.16	97.17	3.48	97.85	2.46	98.87	2.67	98.66*	4.99	96.34	3.33	98.00
P 178	6.6	94.41	5.49	95.52	5.25	95.76	4.76	96.25	5.02	95.99	5.57	95.44*	5.68	95.33	5.75	95.26
W 179	6.7	94.32	4.4	96.62	2.6	98.42	2.15	98.87	2.34	98.68	2.82	98.20*	2.99	98.03	3.78	97.24
P 180	7.83	93.35	2.92	98.26	2.42	98.76	2.06	99.12	2.58	98.60	2.93	98.25*	3.10	98.08	3.36	97.82
W 181	dry	-	5.47	95.64	4.51	96.60	3.96	93.15	2.83	98.28	2.82	98.29*	3.07	98.04	4.18	96.93
P 493	-	-	-	-	-	-	-	-	-	-	-	-	4.10	97.08	3.18	95.86
P 494	-	-	-	-	-	-	-	-	-	-	-	-	5.58	95.31	5.32	95.57
P 495	-	-	-	-	-	-	-	-	-	-	-	-	4.95	96.01	3.72	97.24
P 496	-	-	-	-	-	-	-	-	-	-	-	-	5.36	95.96	5.24	96.08
P 497	-	-	-	-	-	-	-	-	-	-	-	-	3.38	97.91	3.33	97.96
P 498	-	-	-	-	-	-	-	-	-	-	-	-	5.28	96.01	4.96	96.33
P 499	-	-	-	-	-	-	-	-	-	-	-	-	3.98	97.26	3.89	97.35
P 500	-	-	-	-	-	-	-	-	-	-	-	-	2.68	98.52	2.81	98.39
P 501	-	-	-	-	-	-	-	-	-	-	-	-	4.85	96.28	4.68	96.45
P 502	-	-	-	-	-	-	-	-	-	-	-	-	4.82	96.28	4.51	96.59
P 503	-	-	-	-	-	-	-	-	-	-	-	-	4.85	96.42	4.58	96.69

* Well bailed dry after water level recorded.

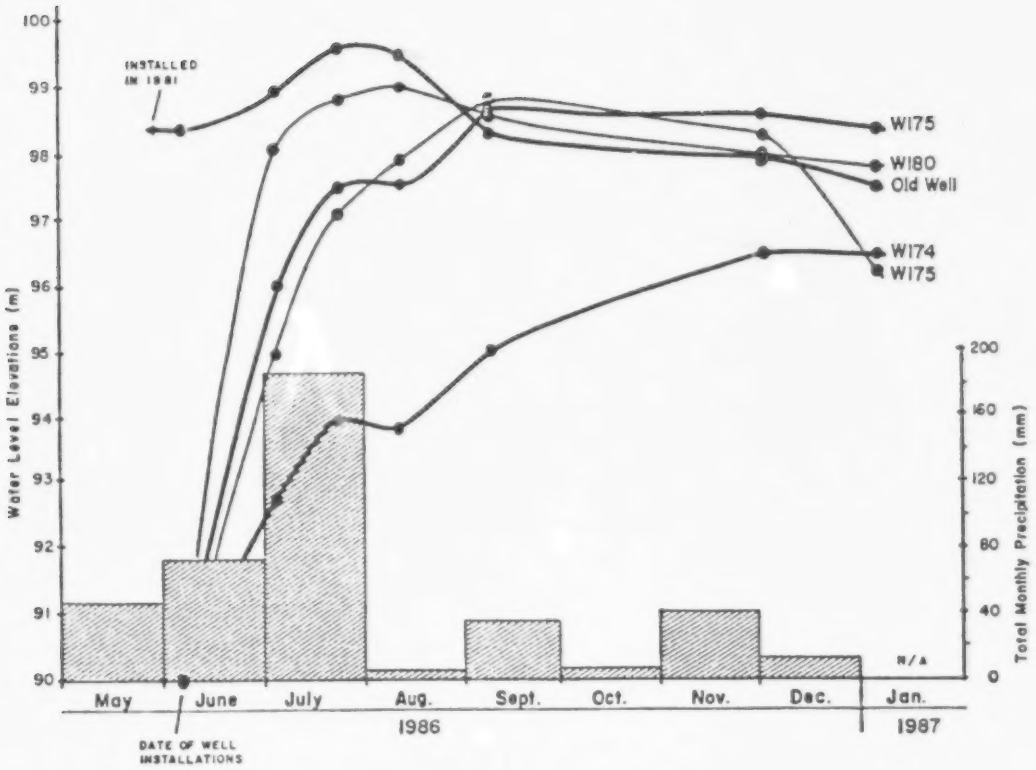


Figure 19. Groundwater level fluctions and precipitation at Lloydminster.

5.3.3 Chemistry

5.3.3.1 Sludge composition. Establishing the inorganic and organic chemistry of the waste sludge is an important prerequisite to identifying potential contaminants. Mixtures of sludges from three different companies in the Lloydminster area were selected for landtreatment. Sludge was applied to all the plots on July 8, 1982 and to west half of plots on May 4, 1983. The sludges, mixtures of sand and heavy oil, contained on the average 11% oil, 4% water and 85% solids, with an average pH of 8.5 (Peake et al. 1984). Slopoil was applied to all the plots in 1984 and 1985, but data for these materials are not available.

Neutral nitrogen, resins and asphaltenes, which are relatively resistant to microbial degradation, made up a large proportion of the original sludge (Peake et al. 1984). The average inorganic and metal composition of sludges used for landtreatment at the site is summarized in Table 25. One of the most diagnostic characteristics of the sludge was the extreme variability in the inorganic composition. The aqueous portion of the sludge, which consisted primarily of saline formation water, had an average sodium and chloride concentration of 3300 and 2400 $mg \cdot L^{-1}$ respectively.

5.3.3.2 Groundwater chemistry. Groundwater samples were collected for chemical analysis from the old well and monitors installed in June 1986, on September 11, and December 3, 1986, and from all monitors on January 6, 1987. Prior to sampling, monitors were properly purged to ensure samples were representitative of formation water. Samples were collected using a bailer and filtered in the field using a 0.45 mm filter. A list of parameters analyzed for and preservation techniques used is given in Appendix Table 6. Samples were analyzed by the Alberta Environment, Soil Protection Branch laboratory in Lethbridge.

Analytical data (Appendix Tables 7 and 8) indicate that shallow groundwater chemistry is highly variable, reflecting the complex mineralogy of the till. To a depth of approximately 6 m, groundwater varied from the calcium/magnesium-bicarbonate to the calcium/magnesium - sulphate type. The total dissolved solids concentration (TDS) varied from 480 to 7000 $mg \cdot L^{-1}$, with a mean of

Table 25. Inorganic and metals composition of sludges.[1]

INORGANICS ($mg \cdot L^{-1}$)					
Ca	Mg	Na	K	Fe	Mn
7000	3400	3700	1919	10700	350

METALS ($mg \cdot L^{-1}$)					
Cu	Zn	Pb	Cr	Ni	Cd
10	31	23	41	26	0.5

[1] From Peake et al. 1984.

3000 $mg \cdot L^{-1}$. Groundwater from the piezometers completed at the 9 m depth was the calcium/magnesium - sulphate type with a TDS concentration varying from 2500 to 4100 $mg \cdot L^{-1}$.

Total organic carbon (TOC) concentrations in the groundwater varied from 10 to 50 $mg \cdot L^{-1}$, with a mean of 25 $mg \cdot L^{-1}$. This indicates that groundwater has a relatively low organic load.

Detailed information about shallow groundwater chemistry prior to establishment of the plots is not available. However, two samples collected from a well installed prior to sludge-nutrient application were analyzed for key indicators of contamination (Peake et al. 1984) (Table 26).

Table 26. Groundwater chemistry before sludge application.[1]

Date	TC	VOC	TOC	Cl	NO_3	SO_4	pH
82/06/22	190	53	67	3.0	0.1	2830	7.0
82/07/08	164	35	48	1.8	0.1	2680	7.0

[1] From Peake et al. 1984

A comparison of 1986-87 analytical data to pre-sludge application groundwater chemistry data indicates that the chloride and nitrate levels have increased substantially, suggesting groundwater contamination. The probable source of the chloride and nitrate is from the aqueous portion of the sludge and nutrients applied to the site, respectively. Additional monitoring data are required to establish temporal variations in contaminant concentrations and to identify other contaminants.

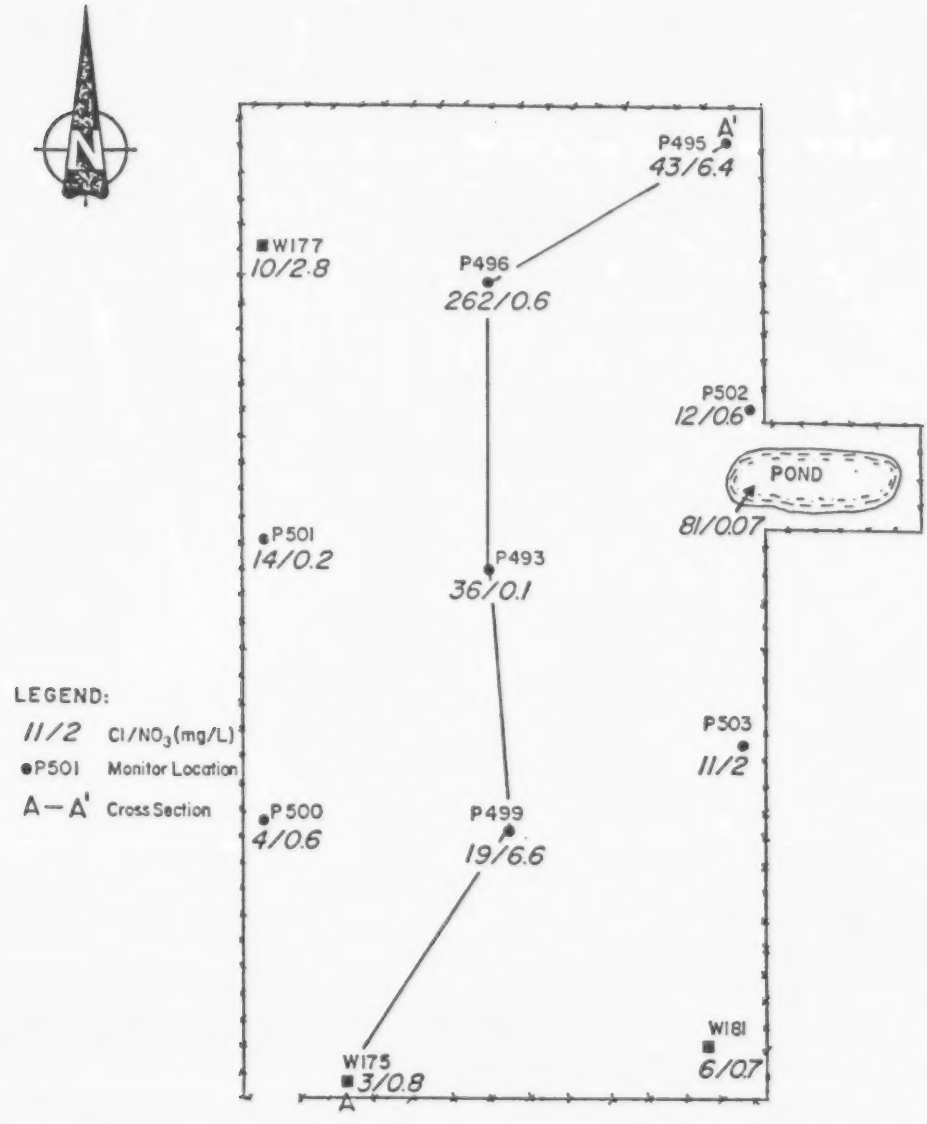
The chloride ion was used to obtain information about the areal extent of groundwater contamination. Chloride is a suitable indicator because it had a low ambient concentration at the site (<10 $mg \cdot L^{-1}$) and is relatively inert and extremely mobile in the aqueous environment. Figure 20 indicates that shallow groundwater

is contaminated beneath and down gradient from the plots. Groundwater tends to be more contaminated in the eastern half of the plots, probably since this area received two applications of sludge. Nitrate levels also tended to be higher in the east half of the plots (Figure 20). The large amount of sludge applied to the east half of plot 8 (in the northeast corner of the demonstration plots) may account for unusually high chloride levels in groundwater from P 495 and W 179.

Groundwater contamination tended to decrease rapidly with depth (Figure 21). This reflects the strong attenuation capacity of the surficial materials. Numerous biological, physical and chemical processes are important in retarding the movement of contaminants from the site. Additional analytical data are required to identify these processes and their importance in contaminant attentuation.

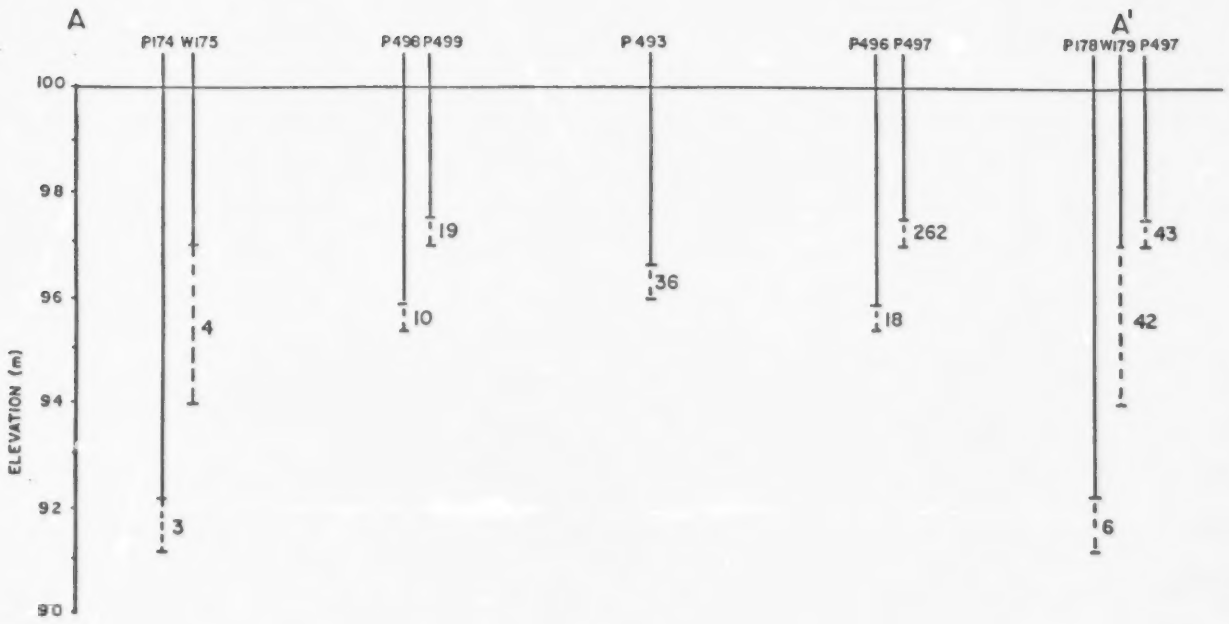
In general, shallow groundwater is of poor quality with several parameters exceeding upper limits established in Canadian Drinking water standards (C.D.W.S.) (Anomymous 1978) (Table 27). It is interesting to note that the lead concentration in groundwater exceeded the CDWS in every analysis. It is uncertain whether this is a natural occurrence or attributable to contamination. The fact that the concentration of other metals, with the exception of manganese levels which are commonly high in groundwater from till, are significantly below CDWS, suggests that contamination is not the source of the elevated lead levels. Additional analysis will be required to resolve the uncertaintly.

5.3.3.3 Surface water chemistry. A sample collected from the runoff pond, prior to sludge application in 1982, was analyzed for key indicators of contamination. The analysis (Table 28) indicates that the water had a very low organic and inorganic load. Immediately after application of the sludge and nutrients the concentrations of chloride, nitrate and sulphate increased dramatically (Figure 22). The analysis of a pond water sample collected on November 4, 1986 indicates that the concentration of chloride, nitrate and sulphate have decreased since the last sludge-nutrient application in 1983. Levels of chloride were much lower in 1986 then in October 1985 (890 ppm), sulphate was also reduced and nitrate was very low in both 1985 and 1986.



ANALYSIS DATE: JAN. 6, 1987

Figure 20. Areal distribution of chloride and nitrate concentrations in shallow groundwater (87/01/06) at Lloydminster.



LEGEND:

P174	WELL NUMBER
19	CHLORIDE CONCENTRATION (mg/L)
⋮	OPEN INTERVAL
A–A'	CROSS SECTION REFERENCE

Figure 21. Chloride concentrations in groundwater at different depths at Lloydminster.

Table 27. Comparison of 86/09/10 groundwater analysis to C.D.W.S.

	Minimum $mg \cdot L^{-1}$	Mean $mg \cdot L^{-1}$	Maximum $mg \cdot L^{-1}$	C.D.W.S.[1] $mg \cdot L^{-1}$
Ca	135	412	570	200
Mg	54	240	608	150
K	4	11	15	N/A
Na	18	348	2024	270
NO_3	0.1	3	12	10
Cl	2	112	815	250
SO_4	96	1700	3650	500
HCO_3	142	487	636	N/A
T. Alk.	342	450	552	N/A
TDS	607	2700	5300	1000
Mn	0.01	0.7	3	0.05
Fe	0.09	0.15	0.2	0.3
Cu	0.01	0.02	0.03	1
Pb	0.12	0.17	0.2	0.05
Zn	0.02	0.03	0.04	5

[1] Canadian Drinking Water Standards

Table 28. Analysis of pond water prior to sludge application[1].

Date	TC	VOC	TOC	Cl	NO_3	SO_4	pH
			$mg \cdot L^{-1}$				
82/07/08	30	0.9	17	1	4.6	3.2	7.4

[1] From Peake et al. 1984.

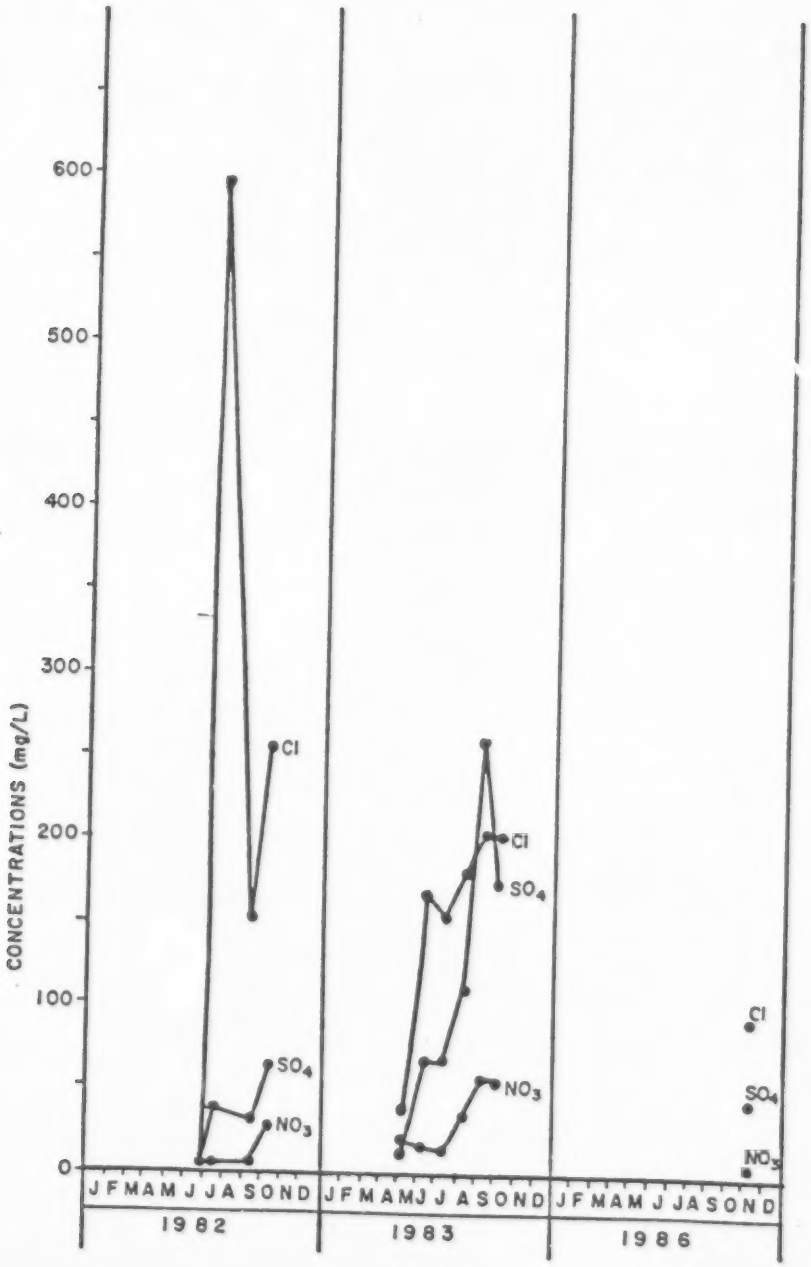


Figure 22 Chloride, nitrate, and sulphate concentration variations in runoff pond water at Lloydminster.

5.4 CONCLUSIONS

The demonstration plots are underlain by relatively low permeability silty clay till to a depth of at least 9 m. Fractures were detected in the till to a depth of approximately 2.5 m.

The predominant direction of shallow groundwater flow is to the east-northeast. More quantitative information about groundwater flow will be possible when water levels reach equilibrium.

Shallow groundwater beneath and down gradient from the plots is contaminated, primarily with inorganic constituents. The contamination decreased rapidly with depth. Water in the surface runoff pond is also contaminated. Contaminant concentrations in surface water increased rapidly after precipitation events.

6. RECOMMENDATIONS FOR FUTURE WORK

1. No more oil wastes should be added to plots at any of the four sites. Emphasis should be placed on means of rehabiltating the sites rather than further overloading the soil systems.
2. Lloydminster should be retained as the high priority study area with emphasis placed on determining soil parameter values that will be predictive of plant performance.
3. The Lloydminster plots should be planted in the spring of 1987 with the same crop that is being planted in the adjacent agricultural field.
4. All 16 plots plus the border area and the adjacent field (a total of 18 plots) should be quantitatively sampled for plant biomass, soil oil content and SAR and soil chloride content. These data should be used to determine factors limiting the growth of crops on the Lloydminster soil. Amounts of chloride should be measured throughout the rooting zone in a limited number of plots.
5. If a patchy distribution of plants is present within the plots, plant and soil samples should be taken to determine if localized differences in oil and chloride contents can be detected and related to plant growth.
6. Further quantitative estimates of hay production at Drayton Valley should be considered in the second year of growth. Residual oil contents should also be measured in conjunction with plant biomass to establish if critical levels can be established.
7. Plots at Grande Prairie and Brooks should be visually assessed to determine if plant growth was more successful in the second year after planting than in the first year and if growth-oil treatment patterns are evident.
8. Methods for assessing plant uptake of potentially toxic oil residues should be further developed and refined and the potential risks from aromatic hydrocarbons in crop plants be evaluated.

9. A small greenhouse study should be conducted on the soils from Lloydminster to determine the potential for the growth of two crops varying in chloride or sludge sensitivity under near optimum moisture and light conditions.
10. From wells established in 1986, data should be collected on hydraulic conductivity to estimate groundwater flow rates and water levels should continue to be monitored.
11. Surface water and groundwater should continued to be monitored for organic contamination and for chloride, nitrate and lead and routine chemical parameters.
12. Plant material at Lloydminster should be analysed for heavy metals to determine if crops are safe for human and animal consumption.
13. A sample of asphaltenes from a plot in Lloydminster which has received heavy sludge treatment should be chemically degraded to identify potentially toxic and mobile constituents that may be expected to be released through the natural biodegradation process. This study would allow the compilation of list of target compounds to be used in the analysis of plants and groundwater for organics.

7. LITERATURE CITED

Anomymous. 1978. Guidelines for Canadian Drinking Water Quality. Health and Welfare Canada.

Coates, J., A.W. Elzerman and A.W. Garrison. 1985. PAH uptake by plants: Methodology and initial investigations. U.S. Environmental Protection Agency Report, Environmental Research Laboratory, Athens, GA.

Peake, E., D. Connery, D. Holowachuk, and W. Weibe. 1984. Land treatment for the disposal of oily waste sludges. Report to Alberta Environmental Research Trust.

Peake, E., D. Connery, D. Holowachuk and W. Weibe. 1985. Land treatment for the disposal of oily waste sludges. Report to the Canadian Petroleum Association and Alberta Environmental Research Trust.

Peake, E. and D. Connery. 1986. Land treatment for the disposal of oily waste sludges in the Lloydminster area, Alberta. Report to Sask-Alta Waste Disposal Co-op.

8. APPENDIX TABLES

Appendix Table 1. Electrical conductivity (E.C.), sodium adsorption ratio (SAR) and chloride, sodium, and sulphate concentrations in saturated extracts of individual samples from Lloydminster oily sludge plots.

Sample		E.C. ($ds.m^{-1}$)	SAR	Chloride ($me.L^{-1}$)	Sodium ($me.L^{-1}$)	Sulphate ($me.L^{-1}$)
Control	1	2.0	4.0	11.5	9.4	3.5
	2	2.8	5.0	18.0	13.6	5.3
	3	2.7	3.4	17.9	9.8	4.9
	4	2.8	3.0	18.0	9.3	6.5
	5	2.8	2.4	18.0	7.9	6.5
1W	1	1.8	4.5	8.5	9.9	4.2
	2	2.5	5.6	14.0	14.5	5.9
	3	3.4	7.2	19.8	20.4	8.9
	4	3.4	6.2	21.8	18.1	6.6
	5	3.2	7.2	17.3	19.8	8.9
4W	1	3.8	5.5	23.3	18.6	6.2
	2	6.0	6.8	43.8	28.8	13.5
	3	5.4	6.5	38.3	25.9	13.0
	4	6.1	6.6	44.3	28.9	15.0
	5	2.6	4.5	13.0	12.9	8.6
5W	1	6.3	6.5	47.0	28.8	13.5
	2	5.1	6.4	33.0	24.9	13.0
	3	3.0	4.8	14.3	14.8	9.2
	4	3.8	4.6	19.8	16.6	12.7
	5	2.9	4.4	12.3	13.8	10.9
8W	1	--	--	--	--	--
	2	1.2	2.8	3.5	5.8	3.9
	3	1.2	2.2	3.8	4.8	4.3
	4	1.3	2.7	1.6	5.8	6.2
	5	1.4	2.5	4.3	5.9	5.9

Appendix Table 2. Monitoring Well Completion Information.

Well Number	Date Installed	Well Depth (m)	Height of pipe above ground surface (m)	Screened interval (m)	Ground Elevation (m)	Elevation of pipe (m)
P 174	June 4/86	8.8	0.87	1	100.25	101.12
W 175	June 4/86	6.0	0.97	3	100.18	101.15
P 176	June 4/86	9.0	0.93	1	100.30	101.23
W 177	June 4/86	6.0	1.03	3	100.30	101.33
P 178	June 4/86	8.8	0.97	1	100.04	101.01
W 179	June 4/86	6.0	1.01	3	100.01	101.02
W 180	June 4/86	8.8	0.97	1	100.21	101.18
W 181	June 4/86	6.0	1.02	3	100.09	101.11
P 493	Dec 3/86	4.0	1.05	0.62	100.13	101.18
P 494	Dec 3/86	4.6	0.95	0.50	99.94	100.89
P 495	Dec 3/86	3.0	1.05	0.50	99.91	100.96
P 496	Dec 3/86	4.6	1.05	0.50	100.27	101.32
P 497	Dec 3/86	3.0	1.05	0.50	100.24	101.29
P 498	Dec 3/86	4.6	1.02	0.50	100.27	101.29
P 499	Dec 3/86	3.0	0.98	0.50	100.26	101.24
P 500	Dec 3/86	4.3	1.10	0.50	100.10	101.20
P 501	Dec 3/86	4.3	1.05	0.50	100.08	100.13
P 502	Dec 3/86	4.3	1.05	0.50	100.05	101.10
P 503	Dec 3/86	4.3	1.04	0.50	100.23	101.27
Old Well	1983	11.0	0.93	?	100.00	100.93

Appendix Table 3. Groundwater Protection Branch Drill Hole Log, June 4, 1986.

Land Location SE Sec. 10 Tp. 50 R. 1 W. 4

Date: June 4, 1986 Supervisor: Ceroici/de Brentani

Project: Lloydminster Oil Sludge Plots (Landtreatment)

Test Hole: 174 to 181 inclusive

Test Hole: 174

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.[1]
0.0-4.0	till	sandy to silty clay, brown, dense, some pebbles	d
4.0-6.0	till	sandy to silty clay, grey, some small pebbles	sm
6.0-7.5	till	sandy to silty clay, grey, very dense, some iron oxide staining	m
7.5-9.0	till	sandy to silty clay, grey, very dense, some thin, fine grained sand lenses	m
TH 175			
0.0-6.0	same as #174		
TH 176			
0.0-3.0	till	sandy to silty clay, brown, dense some pebbles, thin sand lenses, fractures containing calcium compounds, some iron oxide staining	sm
3.0-4.0	till	sandy to silty clay, brown, very dense	sm
4.0-8.0	till	sandy to silty clay, grey, very dense	sm
TH 177			
0.0-6.0	same as #176		

Completion: watertable well, 6 m deep
3 m slotted, 55 mm dia. PVC pipe casing

[1] Moisture Content: d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

continued....

Appendix Table 3. (Concluded).

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.[1]
TH 178			
0.0-4.0	till	sandy to silty clay, brown, dense, some pebbles, iron oxide staining, fractures containing calcium compounds	d
4.0-6.0	till	sandy to silty clay, grey, dense	sm
6.0-9.0	till	sandy to silty clay, grey, dense, thin fine grained sand layers, iron oxide stains	s
TH 179			
0.0-6.0	same as #178		
TH 180			
0.0-3.0	till	sandy to silty clay, brown, slightly pliable, some sandy lenses and pebbles	sm
3.0-7.0	till	sandy to silty clay, grey brown, dense, some thin sand layers	sm
7.0-7.5	sand	fine grained, brown	m
7.5-9.0	till	silty clay, grey, pliable	s
TH 181			
0.0-6.0	same as #180		

[1] Moisture Content: d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

Appendix Table 4. Groundwater Protection Branch Drill Hole Log, December 3, 1986.

Land Location SE Sec. 10 Tp. 50 R. 1 W. 4

Date: December 3, 1986 Supervisor: Ceroici/de Brentani

Project: Lloydminster Oil Sludge Plots (Landtreatment)

Test Hole: 493 to 503 inclusive

Test Hole: 493

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.[1]
0-0.2	topsoil	dark brown, loose, hydrocarbons, some veg. materials	m
0.2-1.5	till	silty clay, light brown, plastic, some pebbles	m
1.5-2.0	till	silty clay, light brown, plastic, iron stains, calcite fractures	m
2.0-4.0	till	silty clay, grey brown, crumbly, calcite fractures, thin, fine grained sand streaks	m
TH 494			
0-0.2	topsoil	dark brown, loose, hydrocarbons	m
0.2-1.5	till	sandy to silty clay, light brown, some weathering, pebbles	m
1.5-4.6	till	sandy to silty clay, dark brown, pebbles	m
TH 494			
0-3.0	same as TH 494		
TH 496			
0-0.1	topsoil	dark brown, clayey	sm
0.1-1.2	till	sandy clay, light brown, firm coarse sand and pebbles	sm
1.2-3.0	till	silty clay, grey brown, firm, pebbles	sm
3.0-4.5	till	silty clay, darker, firm, pebbles	sm

[1] Moisture Content: d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

continued....

Appendix Table 4. (Continued).

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.[1]
TH 497			
0-3.0	same as TH 496		
TH 498			
0-1.5	till	silty clay, brown, firm, some calcite streaks, small pebbles	sm
1.5-3.0	till	silty clay, darker, firm, pebbles	sm
3.0-4.5	till	silty clay, grey brown, firm, some pebbles and stones	m
TH 499	same as TH 498		
TH 500			
0-1.5	till	silty clay, dark brown, firm calcite streakes, pebbles	sm
1.5-3.7	till	silty clay, dark brown, firm few pebbles	m
3.7-4.3	sand	silty-fine grained, light brown	s
TH 501			
0-0.5	till	silty clay, brown, firm	sm
0.5-1.5	till	silty clay, dark brown, firm, calcite streaks	sm
1.5-4.3	till	silty clay, dark brown, firm, some pebbles	m

[1] Moisture Content: d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

continued....

Appendix Table 4. (Concluded).

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.[1]
TH 502			
0-1.0	till	silty clay, dark brown, firm, some pebbles	sm
1.0-1.5	till	silty clay, dark brown, firm, calcite streaks	sm
1.5-4.3	till	silty clay, dark brown, firm, some pebbles	m
TH 503			
0-1.0	till	sandy clay, dark brown, firm	sm
1.0-1.5	till	silty clay, grey brown, firm, calcite streaks	sm
1.5-4.3	till	silty clay, grey brown, firm, few pebbles	sm

[1] Moisture Content: d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

Appendix Table 5 Core Description Test Hole #493

DEPTH (m)	DESCRIPTION
0-0.15	soil, clayey, black, hydrocarbon staining, some roots
0.15-0.46	clay, brown, compact, contains pebbles
0.46-1.10	till, clayey, brown, very dense, plastic, some pebbles, iron stain streaks
1.10-1.52	till, clayey, brown, very dense, plastic, pebbles, fractures visible, calcite on fracture faces (acid test-positive)
1.52-1.83	till, clayey, brown, plastic, pebbles, calcite and iron staining on fracture faces
1.83-2.44	till, clayey, brown-grey, pebbles, less plastic, fewer fractures
2.44-3.05	till, clayey, brown-grey, pebbles, crumbly, contains fine grained sand lenses about 5 mm thick
3.50-4.12	till, clayey, brown-grey, pebbles (some coal specks), very dense, plastic, iron stain streaks

Appendix Table 6 List of Chemical Parameters and Preservation Techniques.

Chemical Parameter	Method of Preservation
Inorganic	
Cl, SO_4, HCO_3, NH_4, Na, K, Ca, Mg	- 250 ml plastic bottle - refrigerate
Organic	
COD	- 125 ml plastic bottle - acidify 5 ml H_2SO_4 - refrigerate
TOC	- 125 ml plastic bottle - refrigerate
Metals	
Cu, Fe, Mn, Pb, Zn	- 125 ml plastic bottle - acidify 5 ml (1:1) HNO_3 - refrigerate

Appendix Table 6. Lloydminster Groundwater Chemistry: Routine Parameters.

Appendix Table 7 Lloydminster Groundwater Chemistry: Organics, Metals, and Nutrients.

Well Number	Sample Date	pH	E.C. (mS cm^{-1})	S.A.R.	Ion Balance	T.H.	Ca	Mg	K	Na (mg L^{-1})	Cl	SO_4	HCO_3	T.A.	T.D.S.
W181	03/12/86	7.53	3.02	0.60	1.00	2055	472	213	7.8	59.8	4.4	1704	497	408	2730
P180	03/12/86	7.16	3.91	1.80	1.00	2400	542	254	14.1	209.3	0.0	2256	644	528	3610
W179	03/12/86	7.48	1.82	0.60	1.01	940	204	104	4.3	39.1	230.4	302	477	366	1130
P178	03/12/86	7.07	2.89	0.70	1.00	1925	440	200	10.9	66.7	3.6	1536	576	472	2540
W177	03/12/86	7.43	5.63	2.20	1.00	3770	516	603	14.5	310.5	10.6	3744	629	516	5530
P176	03/12/86	7.09	4.30	1.70	0.99	2780	542	346	16.4	202.4	8.0	2736	517	424	4110
W175	03/12/86	7.53	0.94	0.30	1.01	550	131	53	6.3	18.4	3.6	108	566	464	612
P174	03/12/86	7.01	2.92	0.60	1.01	2000	498	183	12.9	59.8	2.7	1536	640	525	2610
OLD-W	03/12/86	7.55	3.40	1.40	1.01	1360	276	164	4.3	119.6	744.5	134	467	382	1740
LAGOO	04/11/86	6.94	0.54	1.90	1.01	160	44	12	3.5	57.4	80.6	43	151	124	314
W177	11/09/86	7.91	5.50	2.17	0.98	3550	420	608	15.2	296.7	12.4	3648	580	476	5316
W180	11/09/86	8.03	2.85	0.56	1.03	1900	468	199	8.2	57.5	4.4	1584	461	378	2580
P181	11/09/86	7.83	3.84	1.80	1.04	2456	552	261	13.7	204.7	11.5	2070	636	522	3541
OLD-W	11/09/86	7.85	3.30	1.63	1.03	1450	314	161	3.9	142.6	815.0	141	454	377	1857
P176	11/09/86	7.70	4.35	1.63	1.03	2925	570	365	15.6	202.4	8.0	2736	534	438	4162
P178	11/09/86	7.68	2.87	0.63	1.02	1975	458	202	10.9	64.4	1.9	1560	572	468	2581
W179	11/09/86	7.95	1.70	0.48	1.01	853	180	98	4.3	32.2	257.0	196	417	342	987
P174	11/09/86	7.67	2.96	0.53	1.03	2075	504	189	12.5	55.2	4.4	1584	600	493	2655
W175	11/09/86	8.04	0.95	0.34	1.04	560	135	53	5.9	18.4	3.5	96	568	466	607
P500	06/01/87	8.13	2.14	1.10	1.03	1300	250	162	6.6	92.4	3.5	826	725	594	1710
P501	06/01/87	7.99	4.09	1.30	1.01	3000	500	420	12.5	164.0	14.1	2565	409	334	4190
P502	06/01/87	7.68	3.04	0.60	1.00	2250	540	216	10.6	69.3	11.5	2064	270	222	3090
P496	06/01/87	7.51	4.82	2.80	1.00	3000	500	480	15.6	360.4	17.7	3312	382	314	482
P495	06/01/87	7.82	1.80	0.70	1.02	1075	230	120	5.1	55.4	43.4	806	328	268	1460
P489	06/01/87	8.00	1.17	0.40	1.01	700	180	60	7.4	23.1	9.7	401	400	328	881
P497	06/01/87	7.99	6.49	2.90	0.99	4500	560	744	10.9	452.8	261.6	4493	516	423	6870
P493	06/01/87	7.68	1.63	1.00	0.96	925	210	96	7.8	67.0	36.3	463	739	606	1250
OLD-W	06/01/87	7.50	2.30	1.00	0.98	1160	220	132	4.3	73.9	496.0	113	506	414	1370
P494	06/01/87	7.72	3.03	0.80	0.98	2125	510	204	10.2	85.5	15.1	2006	320	262	3000
W181	06/01/87	7.64	3.17	0.80	1.00	2350	530	246	11.3	90.1	6.2	2035	517	424	3180
P180	06/01/87	7.63	3.62	1.80	0.99	2425	550	252	14.5	205.6	12.4	2280	646	530	3640
W179	06/01/87	7.38	1.90	0.70	1.01	1125	250	120	6.3	53.1	141.8	576	509	417	1420
P178	06/01/87	7.31	2.79	0.70	0.99	2000	470	198	11.3	69.3	6.2	1632	583	478	2680
W177	06/01/87	7.49	5.31	2.20	1.02	3700	498	595	14.1	304.9	9.7	3600	631	517	5360
P176	06/01/87	7.12	4.06	1.60	1.02	2800	540	348	16.0	200.9	6.2	2621	565	463	4020
W175	06/01/87	6.92	1.41	0.30	1.02	940	252	75	7.8	23.1	2.7	475	593	486	1130
P174	06/01/87	7.04	2.70	0.60	1.02	1975	480	186	12.9	57.8	3.5	1622	643	527	1370
P503	06/01/87	7.89	0.96	0.60	0.99	540	136	48	5.9	30.0	10.6	288	374	306	714
P499	06/01/87	8.20	0.61	0.40	1.00	345	75	38	4.3	18.5	18.6	41	375	307	412

Appendix Table 8. Lloydminster Groundwater Chemistry: Organics, Metals, and Nutrients.

Well Number	Sample Date	T.O.C.	C.O.D.	NO_3	Fe	Mn	Cu	Pb	Zn
				(mg L^{-1})					
W181	03/12/86	0.0	0	4.76	0.07	0.00	0.00	0.00	0.00
P180	03/12/86	0.0	0	0.07	0.41	0.00	0.00	0.00	0.00
W179	02/12/86	0.0	0	5.18	0.08	0.00	0.00	0.00	0.00
P178	03/12/86	0.0	0	0.07	0.20	0.00	0.00	0.00	0.00
W177	03/12/86	0.0	0	50.4	0.08	0.00	0.00	0.00	0.00
P176	03/12/86	0.0	0	0.07	0.21	0.00	0.00	0.00	0.00
W175	03/12/86	0.0	0	2.80	0.04	0.00	0.00	0.00	0.00
P174	03/12/86	0.0	0	0.07	0.08	0.00	0.00	0.00	0.00
OLD-W	03/12/86	0.0	0	14.70	0.28	0.00	0.00	0.00	0.00
LAGOO	04/11/86	45.0	134	0.07	0.36	0.06	0.01	0.02	0.01
W177	11/09/86	6.1	144	6.65	0.14	0.08	0.03	0.20	0.03
W180	11/09/86	37.6	49	7.00	0.11	0.02	0.02	0.17	0.03
P181	11/09/86	11.3	128	0.07	0.12	0.18	0.02	0.13	0.03
OLD-W	11/09/86	19.7	221	11.62	0.23	0.78	0.02	0.18	0.03
P176	11/09/86	35.0	116	0.14	0.22	2.90	0.02	0.19	0.04
P178	11/09/86	14.9	29	0.07	0.12	0.22	0.02	0.17	0.04
W179	11/09/86	14.6	87	2.87	0.09	0.01	0.01	0.13	0.02
P174	11/09/86	48.9	160	0.07	0.13	1.63	0.02	0.16	0.04
W175	11/09/86	5.5	15	3.36	0.10	0.02	0.01	0.12	0.02
P500	06/01/87	0.0	0	2.80	0.00	0.00	0.00	0.00	0.00
P501	06/01/87	0.0	0	0.21	0.00	0.00	0.00	0.00	0.00
P502	06/01/87	0.0	0	0.63	0.00	0.00	0.00	0.00	0.00
P496	06/01/87	0.0	0	0.63	0.00	0.00	0.00	0.00	0.00
P495	06/01/87	0.0	0	6.44	0.00	0.00	0.00	0.00	0.00
P489	06/01/87	0.0	0	0.21	0.00	0.00	0.00	0.00	0.00
P497	06/01/87	0.0	0	18.76	0.00	0.00	0.00	0.00	0.00
P493	06/01/87	0.0	0	0.07	0.00	0.00	0.00	0.00	0.00
OLD-W	06/01/87	0.0	0	17.57	0.00	0.00	0.00	0.00	0.00
P494	06/01/87	0.0	0	0.21	0.00	0.00	0.00	0.00	0.00
W181	06/01/87	0.0	0	0.70	0.00	0.00	0.00	0.00	0.00
P180	06/01/87	0.0	0	0.07	0.00	0.00	0.00	0.00	0.00
W179	06/01/87	0.0	0	5.04	0.00	0.00	0.00	0.00	0.00
P178	06/01/87	0.0	0	0.07	0.00	0.00	0.00	0.00	0.00
W177	06/01/87	0.0	0	4.55	0.00	0.00	0.00	0.00	0.00
P176	06/01/87	0.0	0	0.07	0.00	0.00	0.00	0.00	0.00
W175	06/01/87	0.0	0	0.84	0.00	0.00	0.00	0.00	0.00
P174	06/01/87	0.0	0	0.07	0.00	0.00	0.00	0.00	0.00
P503	06/01/87	0.0	0	1.89	0.00	0.00	0.00	0.00	0.00
P499	06/01/87	0.0	0	6.58	0.00	0.00	0.00	0.00	0.00